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NIAGARA MEETING OF THE AMERICAN ELECTROCHEMICAL SOCIETY.

The fourth general meeting of the American Electrochemical Society will be held at Niagara Falls on September 17 to 19, the preliminary programme being printed on another page of this issue. A good attendance is assured; for, next to New York City and Philadelphia, Niagara Falls has the largest local membership list, and—which counts probably more— the Niagara members represent a relatively large percentage of those who are building up by hard and steady work the electrochemical industries in this country. Such men are really the heart and soul of a technical society. Moreover, the charm of the Falls is ever fresh, so that the choice of Niagara for this meeting is fully justified, although the opinion which has found expression is not unwarranted that Niagara as a convention city appears to have been somewhat overdone in recent years. Some members may find it unnecessarily inconvenient and expensive to attend the convention of the American Institute of Electrical Engineers at Niagara in July, and the convention of the American Electrochemical Society again in September. In this era of commercial trusts, labor unions and union engineering buildings, a joint meeting of both societies would have been in order, and we regret that practical considerations prevented the realization this time in spite of the good will on both sides.

One special feature of the technical programme of the meeting appears to call for some comment, namely, a general discussion of the electrolytic dissociation theory to which one session is to be devoted. At its last convention the American Institute of Electrical Engineers gave a whole day to the discussion of engineering problems in connection with high-tension power transmission, which proved to be the most successful session of the meeting. We hope the discussion of the dissociation theory will be no less interesting or successful. The theory is now old enough to prevent such misunderstandings as were common when this hypothesis was first placed before the world in a somewhat pronounced and aggressive form. The dissociation theory has, without any doubt, inspired an enormous amount of excellent experimental work, and has thus done much good. Whether it is capable of change or improvement is, of course, another question, and should be a subject for a good discussion. While this subject is a specially attractive one for theorists to talk about, we would like to see practical electrochemical engineers join vigorously in the discussion at Niagara. It would be extremely interesting to hear from practical men what the dissociation theory has done for them, or where it has failed. After all, a theory is nothing but a tool, and its importance is to be estimated from its value as a "working hypothesis." Tools are capable of improvement; but to improve them it is necessary to understand clearly in which respect they are failing.

FACTS CONCERNING ELECTRIC STEEL PROCESSES.

For some time we have given considerable space to the discussion of electric steel processes. While we have gladly opened occasionally our columns to a discussion of future possibilities, yet we have mainly endeavored to disseminate knowledge of what actually has been done, by publishing correct and authoritative information on the work of the various inventors working in the field of electrometallurgy of iron and steel. This issue contains two interesting articles of this character. The one is a paper contributed to our columns by Dr. P. L. T. Héroult, who shares with Mr. Charles M. Hall the credit of having discovered the electrolyte now in universal use for the electrolytic production of aluminium, but whose activity in recent years has been mainly absorbed in improvements in the electrometallurgy of iron and steel. The other is a rather full abstract of a recent paper of Dr. Hans Goldschmidt of "thermite" fame, who gives a review of the present situation of the electrometallurgy of steel, and some especially interesting exact data concerning the product of the Kjellin process, operated at Gysinge in Sweden.

The most important fact to which we call attention is the commercial success of the electric production of high-grade tool steels by Héroult and Kjellin. True, the beginnings are small, but both processes must be considered to be now beyond the experimental stage, since they are working continually and their products find a market. It was, of course, to be expected that electrical processes would achieve their first commercial success in the production of high-grade crucible steels, for the reason that the cost of their preparation by the old method is high, and the chief advantages of electrical methods—cleanliness, flexibility and perfect control—must appear here in the best light. For such purposes contaminations of the metal from the electrodes must be eliminated. Kjellin accomplished this in the most radical way—by using no electrodes at all. The metal forms the single-turn powerful current secondary of a transformer, and the electrical energy supplied to the primary winding appears in the secondary as heat. It would be interesting, however, to determine exactly the amount of magnetic leakage; this might not be inconsiderable in the construction chosen by Kjellin. Héroult uses what he calls "electrodes," but they do not dip into the molten metal and are no electrodes in the ordinary electrochemical sense, being only the terminals of the circuit from which arcs jump over to the molten metal. He obtains the heat mainly from radiation from his powerful arcs, and only to a comparatively small extent in the form of Joulean heat. It may be added that there are other methods available by which contaminations of the metal from carbon electrodes might be avoided.

A brief remark in Dr. Héroult's article is especially worthy of attention, namely, that his process will soon be applied for the production of the best grade of tool steels in connection with a large blast furnace works where electricity will be produced by a blast furnace gas motor. This short note appears to indicate the lines along which commercial electrometallurgy of steel will probably develop. It is not probable that the electric furnace will soon supersede the blast furnace in general, but for special work, like the production of special high-grade kinds of steel, the electric furnace has proven to be a commercial success, and appears to have come to stay. It seems quite probable that in future electric furnaces will be operated side by side with blast furnaces, not in competition, but in co-operation with them. The splendid development of gas engines in recent years has made possible and practical the utilization of blast furnace gases—which are still wasted to a great extent—for the generation of electrical energy; and it would seem only a logical development to utilize this electrical energy for the operation of electric furnaces for special work to supplement the blast furnaces employed in the general ordinary work. While the industrial development of the electrometallurgy of aluminium has been intimately connected with water-power developments, it is quite probable that the future of the electrometallurgy of steel will to some extent be connected with the utilization of the waste gases from blast furnaces.

BLEACHING POWDER AND BLEACHING LIQUORS.

In this issue we publish an interesting article by Dr. W. H. Walker on the various methods in commercial use abroad for producing hypochlorites, or, as they are commonly called, bleaching liquors. The subject is certainly a timely one, in view of the fact that among the larger paper, pulp and textile mills of this country, there is a pronounced tendency to install their own electrolytic plants to produce the bleaching reagents used in their works. In all plants so far installed—the majority of which are in the New England States—diaphragm processes are used for making bleaching powder. This is in distinct contrast with the situation abroad, where a variety of apparatus, as described in Dr. Walker's articles, are in commercial use for the direct production of bleaching liquors.

When Hermite first introduced hypochlorite apparatus into practice in a somewhat undeveloped form, his apparatus was experimented with in several mills of this country, but soon abandoned for the reasons mentioned by Dr. Walker. The only remains in this country of this type of apparatus appears to be a small and rather crude municipal plant in Philadelphia, under control of the Board of Health, the hypochlorite being used for disinfecting purposes. When we visited this plant last year, it was not in operation, for the reason that no funds were available, but it was expected that the plant would again be put in operation later.

The contrast between the situation in this country, and the extended use of hypochlorite apparatus abroad was pointed out by Dr. F. Haber in his report on the electrochemical industry in the United States, which is, and will remain for quite a while, a fertile source for comment and discussion. Dr. Haber points out the reason why our paper and pulp mills prefer to use diaphragm cells, and to make their own bleaching powder. It is simply a matter of cost, since it is considerably cheaper to produce bleaching powder by the diaphragm process than to make strong hypochlorite solutions. What is wanted in pulp mills is usually a solution containing 25 grams of bleaching chlorine per liter; to produce such a strong solution a comparatively great amount of energy is required, for the reason that the ampere-hour efficiency of hypochlorite apparatus is rather low. It is therefore rather improbable that

pulp and paper mills will install hypochlorite apparatus, especially as the diaphragm cells now in use in this country are relatively cheap and efficient apparatus.

The situation is, however, quite different in the case of textile mills, laundries and bleacheries, since weaker solutions and smaller amounts of the same are here required. The great simplicity of operation of hypochlorite apparatus is also a point of importance. Moreover, as Dr. Walker remarks, the color of the finished goods is purer and more even if bleaching liquors are used; the solution penetrates the fibres more easily, giving a color of greater permanence; and there is no danger of the deposition of insoluble calcium salts producing a harsh or rough feeling on the goods. The fact—which we know to be a fact—is therefore not surprising that textile manufacturers of this country are beginning to consider the application of hypochlorite apparatus.

ELECTROLYTIC PRODUCTION OF WHITE LEAD.

Our Digest of Electrochemical Patents prior to July 1, 1902, deals in the current issue with the electrolytic production of white lead, than which no more intricate and elusive subject is offered for the consideration of the technical electrochemist. The patents, however, give no adequate idea of the difficulties which arise in practice. As a rule the methods of the specifications are extremely simple, and in all cases they are described as cyclical in character; that is to say, the methods require for their indefinite continuance only the supply of the lead, carbon dioxide and water eliminated in the pigment. The principle of nearly all is the electrolytic solution of an anode of lead, and its subsequent chemical separation as basic carbonate by reaction with the alkaline solution from the cathode, supplemented by the action of carbon dioxide introduced into the cell or into a carbonating chamber, which receives the precipitated hydroxide.

The alkali metal nitrates, and acetates are the electrolytes commonly noted. Of these the former requires less e. m. f, owing to its depolarizing effect at the cathode, but its gradual reduction to nitrate and ammonia introduces changes in the composition of the bath, which are by no means negligible, and which correspond to a gradual deterioration in the character of the pigment. The basic carbonate must not only have the proper chemical composition, but it must comply with high commercial requirements as regards its color, its covering power, and its tinctorial effect. In these respects it is sensitive to minute changes of conditions, and the familiar problem of maintaining initially good conditions is here presented in its most serious aspect.

ELECTROLYSIS AT SMOOTH AND PLATINIZED PLATINUM ANODES.

In this issue we publish a highly interesting article by Prof. F. Foerster, in which this distinguished German electrochemist sums up the results of the extended researches made by him and under his direction on electrolysis at smooth and platinized platinum anodes. The familiar phenomenon of "overvoltage" appears here in a new and interesting light. In the present case we have to deal with the development of oxygen at an anode which requires an overvoltage, and the anodic potential required for the generation of oxygen undergoes very peculiar changes during the course of electrolysis. Dr. Foerster shows that there is undoubtedly a change going on in the anode itself, but frankly admits that we do not yet know the exact causes which are at the bottom of the phenomena. Nevertheless, we now know the phenomena as they are, and Dr. Foerster is right in pointing out that our increased knowledge of the facts should help us in improving technical methods. In this connection the researches on the electrolysis of sodium chloride are especially interesting. Even if platinized platinum anodes should not be introduced into practice it is always important to know the ideal conditions for a process, even if they cannot be realized in practice. The technical man then has a goal to strive at, and can try to approach the ideal conditions as much as possible by different and through imperfect, yet practical, means.

RARE METALS.

The recent development of special steels, that is, steels containing unusual and costly elements and possessing particularly valuable properties for particular purposes, is mostly responsible for a revival of interest in many of the rare metals. The result has been a ransacking of all known occurrences of these metals in nature, a general overhauling of the laboratory methods, for their qualitative detection and quantitative estimation, and a diligent search for new and improved methods of industrially extracting the pure metals or their pure compounds.

The discovery of comparatively large deposits of tungsten, molybdenum, vanadium and uranium ores in Arizona, Colorado and Canada, has in recent years made America the chief purveyor of these ores for commercial purposes. Our uranium and vanadium ores are particularly in demand, and regular shipments of these valuable materials are made from Colorado, via New York, to Europe. Unfortunately, we must here confess, that we are, to some extent, buying back these metals, or their alloys, from our European friends, after they have exerted their skill in extracting them from the ores we ourselves furnish.

To ameliorate this condition of affairs, not at all flattering to our American chemists and metallurgists, Mr. A. B. Frenzel, of Denver, offered last April a prize of two hundred and fifty dollars, to be awarded by the Governing Board of the American Electrochemical Society to the person submitting the best paper on "practical methods of treating the rare minerals found in America and extracting the rare metals therefrom"; the donor of the prize further agreeing to furnish free of charge any reasonable quantity of raw material at his disposal, viz., ores of uranium, vanadium, molybdenum and tungsten. We have reason to know that this offer has already greatly stimulated the study of these rare metals, and that many investigators in different parts of America, convinced of the need of careful work in this direction, are now devoting their energies to the problem. Almost coincidently with the occurrences mentioned above, we can record the publication of two American books treating exclusively of the subject in hand. They are analyzed in our columns for Book Reviews in this issue.

NIAGARA FALLS MEETING OF THE AMERICAN ELECTROCHEMICAL SOCIETY.

The fourth general meeting of the American Electrochemical Society will be held at Niagara Falls, N. Y., September 17, 18 and 19, 1903.

The meeting will be held at the Auditorium of the Cataract House, beginning at 9 A. M., Thursday, September 17. Thursday and Friday afternoons will be devoted to visits to power houses and certain of the electrochemical plants which are open to visitors, and to other points of interest in the vicinity. Thursday evening there will be a smoker and entertainment at the Cataract-International, Friday evening a dance and reception at the Cataract House. Saturday evening will be devoted to a trip to Niagara-on-the-Lake, Youngstown and Port Niagara by boat and trolley.

The headquarters will be at the Cataract House. The special rates at the Cataract House and International Hotel are $3.50 to $5.00 per day, American plan. For further information concerning hotels, address the local secretary, Mr. C. L. Collins, 2d, Niagara Falls, N. Y.

The following titles of papers have been announced:

"A New Type of Electrolytic Cell."—P. G. Salom.

"Manufacture of Ferro-Alloys in the Electric Furnace."—Dr. George P. Scholl.

"Electrolytic Copper Refining."—Dr. W. D. Bancroft.

"Electrometallurgy of Gold."—Dr. W. H. Walker.

"Some Theoretical Considerations of Resistance Furnaces."—F. A. J. FitzGerald.

"On the Supposed Electrolysis of Water Vapor."—F. Austin Lidbury.

"Efficiency of the Nickel Plating Tank."—Prof. O. W. Brown.

"Electrolysis of Sodium Hydroxide, by Alternating Current."—Carl Hambuechen.

"A Practical Utilization of the Passive State of Iron."—Prof. C. F. Burgess.

"Theoretical Properties of Free Ions in Solutions."—Dr. E. F. Roeber.

"Berthelot's Law of Electrochemical Action."—C. J. Reed.

Other papers are expected from Dr. J. W. Richards, David H. Browne, Dr. L. Kahlenberg, Prof. C. F. Burgess, A. H. Cowles, and others.

One session of the meeting will be devoted to the discussion of the theory of Electrolytic dissociation, which will be opened by Dr. W. D. Bancroft.

Volume III. of the Transactions of the Society has recently been mailed to the members. On not less than 445 pages a complete report of the proceedings of the third general meeting, held at New York City from April 16 to 18, is given. Besides Dr. Richards' presidential address on Conditions of Progress in Electrochemistry, the volume contains twenty-eight papers, together with a report of the discussion which followed each paper.

As an appendix, Mr. William J. Hammer's lecture on "radium and other radioactive substances with a consideration of phosphorescent and fluorescent substances; the properties and applications of selenium and the treatment of disease by ultra-violet light" is represented.

Presswork and illustrations are highly creditable.

TUNGSTEN, MOLYBDENUM, URANIUM AND VANADIUM IN 1902.

In view of the increased importance of rare minerals in recent years—which led Mr. A. B. Frenzel, of Denver, Col., to offer a price to the American Electrochemical Society for the best investigation on this subject—the following abstract of a report of Dr. Joseph Hyde Pratt to the United States Geological Survey will prove of interest.

The production of crude tungsten ores during 1902 amounted to 183.5 tons, of which not more than a few tons were sold. The production of 1901 was 179 tons of concentrated ore, valued at $27,720. The larger part of the production of 1902 was from Colorado, with a smaller amount from Connecticut. No new localities were developed during 1902.

Almost the entire production of commercial molybdenite was by the Crown Point Mining Company, of Seattle, Washington, from their property in the western part of Chelan County. The production amounted to about 12 tons. The value of the ores is very erratic, the prices quoted varying from $1,500 to $100 per ton.

There was a marked increase in the production of uranium and vanadium minerals in 1902, which, as reported to the survey, amounted to 3810 tons, valued at $48,125, or $12.63 per ton. This, of course, represents the crude ore. In 1901 the production was 375 tons of crude ore. A portion of the uranium ore was treated, giving a concentrated product of 25 tons, which was valued at $8,000, or $320 per ton.

Although it has been determined that these metals have beneficial effects when used in the manufacture of steel, considerable study of them is necessary before their commercial position with respect to one another or to nickel and chromium can be definitely determined. Questions came up as to which of the various irons hardened by them are best adapted for steel drills, for dies and shoes in stamp mills, for car axles, carpenters' tools, etc., as to which will retain the best cutting edge, which will heat the least when in use, and which will make the toughest iron.

PRODUCTION OF BARYTES IN 1902.

The production of crude barytes in 1902, as reported to the United States Geological Survey by Dr. J. H. Pratt, was considerably in excess of that of 1901, amounting to 61,548 short tons, valued at $195,983, as compared with 49,070 tons, valued at $157,844, in 1901, an increase of 12,478 tons in quantity and of $38,139 in value.

The States producing barytes in 1902 were Virginia, North Carolina, Tennessee, and Missouri. Both Virginia and Missouri largely increased their production; in Tennessee there was a large falling off in production.

Whereas barytes was formerly considered as an adulterant in the manufacture of paints, it is now beginning to be recognized that barytes has excellent qualities of its own that make it of value as a pigment. When it is used in combination with white lead or with zinc white these qualities appear to advantage, since its pure white color is permanent and is unaffected by the weather or by gases that in some cases blacken white lead.

PRODUCTION OF CHROMITE IN 1902.

The report to the United States Geological Survey on chromite for 1902, by Dr. Joseph Hyde Pratt, is now in press.

California was the only State producing any chromite during 1902, the quantity being 315 long tons, valued at $4725. This is a decrease of 53 tons in quantity and of $1065 in value, as compared with the production in 1901, which was 368 long tons, valued at $5,790.

The Pacific Coast offers a promising field for the erection of a chemical plant to treat chrome ores for the manufacture of various chromium salts, as these ores can be obtained in California.

With the completion of the railroad from Erwin, Tenn., to Marion, N. C., the chromite deposits of Yancey County, N. C., will undoubtedly be thoroughly exploited and may become producers.

There is a large amount of chromite ore imported each year into this country, the most of which is from Turkey, with smaller amounts from New Caledonia and Canada. The imports of chrome ore and chromic acid in 1902 were valued at $793,712. The principal chromite deposits of Canada are in the vicinity of Black Lake and Colraine, Quebec Province. The Canadian production for 1902 was 900 long tons, valued at $13,000.

ELECTROLYTIC PRODUCTION OF BLEACHING LIQUOR.

BY W. H. WALKER, PH. D.

As long ago as the year 1774 the Swedish chemist Scheele discovered the element chlorine and noticed that it possessed the property of decolorizing organic material. Chlorine in this form soon found application in the arts, especially in the bleaching of paper stock, but as the action was very difficult to regulate much loss was experienced in its use. It was therefore a great step in advance when eleven years later Berthollet found that if a potash solution were used to absorb the chlorine, instead of water, a very superior bleaching solution was obtained. The work was done at Javelle, near Paris, and this solution soon became known as Eau de Javelle. When later the cheaper soda was substituted for potash the solution received the name of Eau de Laborraque. These bleaching solutions were, however, very unstable, and it was not until Tennant of England discovered that dry calcium hydrate could be used to absorb chlorine gas, and that in this form chlorine available for bleaching could be stored and transported that the use of Berthollet's discovery was made generally available.

Contemporary with these developments came the introduction of the Leblanc soda process, with its great production of hydrochloric acid. In order to utilize this by-product the makers of soda became manufacturers of bleaching powder, and this material soon displaced the older directly prepared bleaching liquors.

As early as 1800 Cruikshank had observed that when an electric current was passed through a solution of common salt chlorine was set free at one electrode, and caustic soda was formed at the other. Twenty years later Brandé proposed the utilization of this reaction by allowing these two substances to unite as did Berthollet, and suggested the use of electrolyzed sea water as a bleaching solution. A number of years after this Lardenois prepared a bleaching liquid which he called "electro-chlorigen" by the electrolysis of brine, using a platinum plate as an anode, and a lead plate as a cathode. From this time on a great number of investigators studied this subject, but owing largely to the great cost of electrical energy and ignorance of the secondary reactions which take place in the electrolysis of brine, they all failed in establishing the art upon a practical commercial basis.

Although the reaction which takes place when chlorine is absorbed in caustic soda was early shown to be $2\ NaOH + Cl_2 = NaCl + NaOCl + H_2O$, it was not until very recent years that several factors which obtain during the electrolysis of brine, and which have a marked influence on the result, were fully studied or appreciated. While the systems for producing bleaching liquor electrolytically, to be mentioned later, differ widely in detail, the principles involved are practically identical in each, so that the theory of their action may be studied independently of the apparatus.

The formation of sodium hypochlorite by the action of the chlorine set free at the anode of an electrolytic cell upon the caustic soda formed at the cathode is in itself a quantitative one. In practice, however, the increase of hypochlorite as measured by the amount of electricity sent through the apparatus is found to be a constantly decreasing quantity as the operation is continued. The principal factors active in bringing about this decreasing current efficiency, which must be recognized in the design of an efficient apparatus for the production of hypochlorite, are the following:

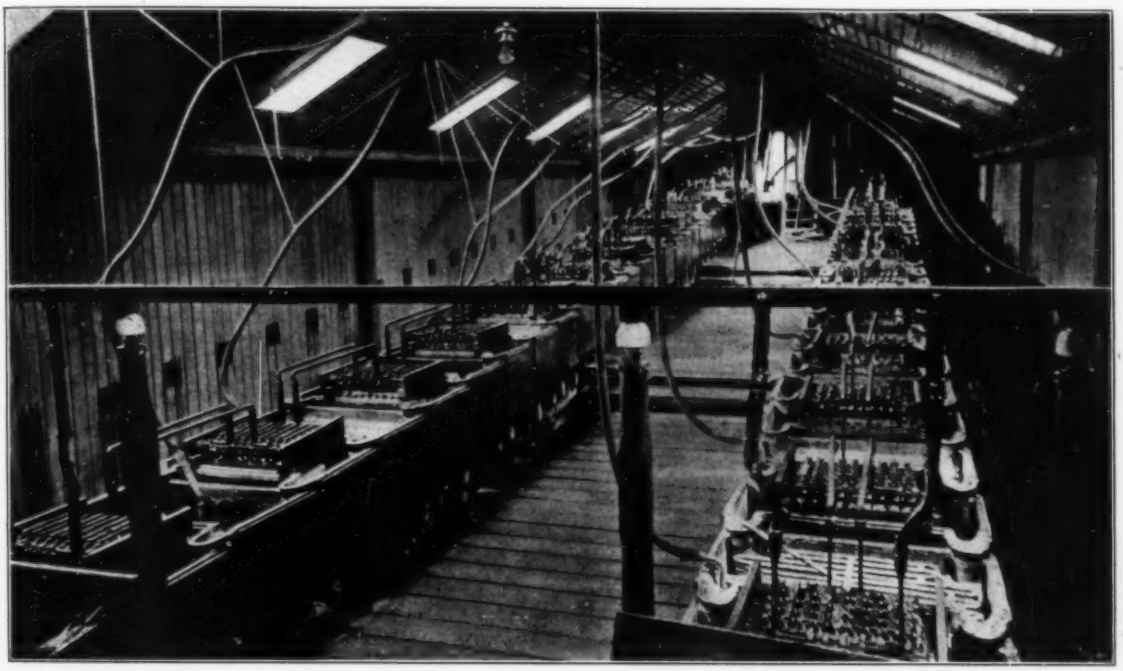


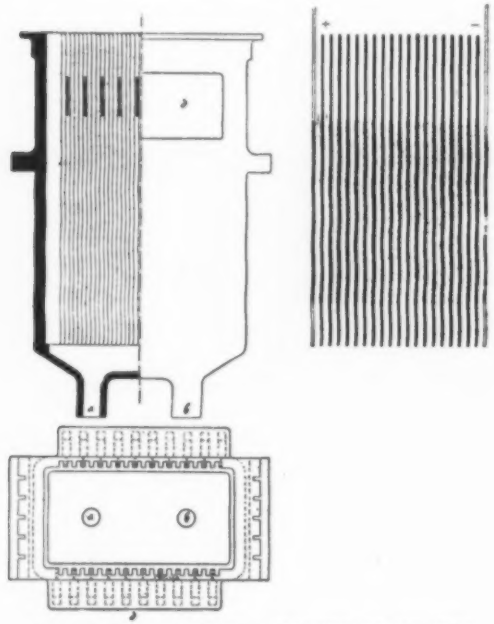
FIG. 1.—INSTALLATION OF SCHUCKERT APPARATUS.

1. So soon as sodium hypochlorite is formed in the electrolyte it commences to take a part in transporting the electric current and the Cl O ions move toward the anode. As the Cl O ions are discharged at a lower potential than Cl ions, all the former, when they reach the anode, receive a positive charge, and, reacting with water, form hypochlorous acid with the liberation of oxygen. This action, with its consequent loss of electrical energy, must become ever greater as the concentration of the electrolyte in hypochlorite increases. That the liberation of oxygen may be reduced to a minimum the anode should be as small as possible compared to the bulk of the electrolyte in order to decrease the opportunity for the Cl O ions to come in contact with the electrode. With an increasing current density, however, the resistance rapidly rises so that too small an electrode means excessive loss in power.

2. Although sodium hypochlorite is relatively stable at ordinary temperatures, it easily breaks up when heated to 50° or 60° C., largely according to the equation $3\ Na\ ClO = Na\ ClO_3$

+2 NaCl. The chlorate thus formed is of no value as a bleaching agent, and the reaction should therefore be prevented by maintaining the temperature of the electrolyte at a low figure. As heat is being constantly generated, both by the passage of the current through the bath, and by the formation of hypochlorite, it is found advisable to provide a cooling system in some part of the apparatus. Since the water used for the purpose is in no way contaminated by its passage through the system, no operating expense is in this way introduced.

3. Hydrogen in its molecular or gaseous state has no reducing action upon hypochlorites; at the moment of its formation on the cathode, however, it rapidly decomposes these compounds with the formation of water, and the corresponding chlorides. It will be seen, therefore, that the sodium hypochlorite in the electrolyte will be destroyed in coming in contact with the cathode in proportion as its amount increases. This difficulty may be in part overcome by employing small cathodes; but, as in the case of the anodes, this reduction in size is limited by the consequent increase in the resistance of the cell. Another method of overcoming the reducing action of the nascent hydrogen is by adding to the electrolyte a substance which will be continuously deposited in the form of a film upon the cathode, and in this way envelop the hydrogen as set free, until it forms bubbles of molecular gas and passes out of the solution. The hydrates of calcium and magnesium act to a certain extent in this way; later developments along this are the patents of Imhoff for the use of chromates and aluminates, and of Schuckert & Co. for the addition of sodium resinate to the brine to be electrolyzed.



FIGS. 2, 3, 4.—SIEMENS & HALSKE APPARATUS.

The strength of salt solution which is most economical to electrolyze, depends upon the amount of available or active chlorine, which it is desirable a litre of the resultant bleaching solution should contain, and on the relative local cost of salt and electrical energy. In general it may be said that raising the concentration of the salt solution lowers the resistance of the bath, increases the current efficiency, and thus for a given yield of chlorine decreases the consumption of energy; it increases, however, the consumption of salt. Complete mixing of the products set free at each electrode is, of course, necessary to prevent the escape of the chlorine before it has had opportunity to react with the caustic soda; in other words the electrolyte must circulate freely within the apparatus.

Every few hours the direction of the curent should be reversed in order that the accumulated insoluble hydrate on the cathodes may be dissolved away; otherwise the resistance is abnormally increased.

The first system for producing bleaching liquor on a commercial scale to be even moderately successful was that of Hermite, introduced in 1884. His apparatus in its final form consisted in a rectangular box of galvanized iron around the top of which ran a trough or channel to carry away the overflow of liquor fed in through a perforated pipe at the bottom. Two shafts ran through the box, carrying numerous discs of zinc, which dipped into the liquor and together with the box formed the cathode of the system. In the space between each pair of discs was a lead form supporting a platinum gauze; these were connected together and formed the anodes. At first it was thought necessary to electrolyze a solution of magnesium chloride, but later it was found that equally good results could be obtained by using common salt, which carried a small quantity of this compound. This process was given extensive trial in America at the soda pulp mill of the Forest Paper Co., of Maine, and at Cumberland Mills, Maine, at the plant of S. D. Warren & Co. Great difficulty was experienced in maintaining the relatively high content of available chlorine necessary to bleach cellulose derived from wood, so, after a year or so both plants were dismantled. We understand, however, that in Norway and Sweden there are in operation several mills which are using this process very successfully.

The only other system which has had extensive trial in America is that of Woolfe, designed to furnish liquor to be used for both bleaching and disinfecting purposes. This process is little more than a crude and comparatively inefficient form of the Hermite process, and after being for some time in operation at the plant of the Duncan Paper Co., Mechanicsville, N. Y., and one or two mills in Pennsylvania, it was finally abandoned.

In Europe, however, greater success has met the attempts to compete with bleaching liquor made from dry chloride of lime. Soon after the work of Hermite, Carl Kellner, a pioneer in the electrolysis of brine, patented a number of processes and types of apparatus for making sodium hypochlorite. The form which Kellner's ideas have finally taken, and which has been perfected and put upon the market by Siemens & Halske, of Vienna, is as follows. A glazed stoneware vessel seen in two sections in Figs. 2 and 3 is divided into a number of small compartments by glass plates fitting into small grooves in its side. These plates are wound with platinum iridium wire, as shown in Fig. 4, and form bipolar electrodes from which the current passes in series through the solution in each compartment. There are holes in the bottom of the vessel through which the brine enters and overflow spouts at the top from

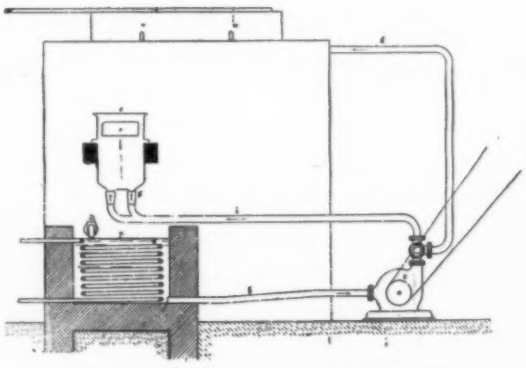


FIG. 5.—SIEMENS & HALSKE APPARATUS.

which the electrolyzed solution flows. Directly under the electrolyzing apparatus is placed a tank provided with a cooling coil of lead pipe, as shown in Fig. 5. The cooled solution is continually raised from the tank to the electrolyzer by the hard lead centrifugal pump, and after passing the electrodes falls again to the cooling tank. This circulation is continued until the content of available chlorine has reached the desired figure, when, by turning a three-way cock the finished bleach solution is forced to the storage reservoir above. Siemens & Halske own the Imhoff patents already referred to, and have recently

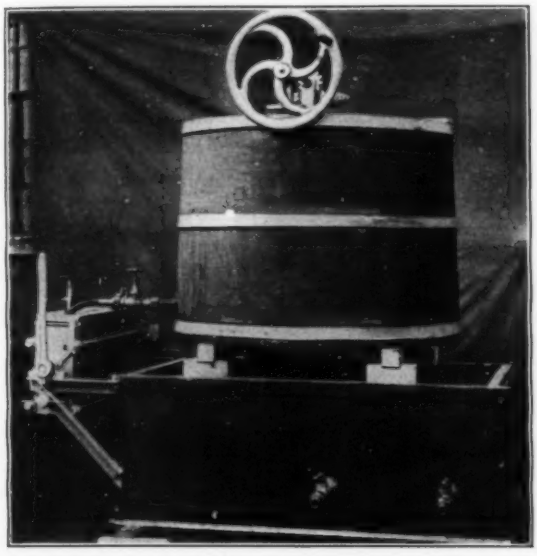


FIG. 6.—HAAS AND OETTEL APPARATUS.

made improvements in the apparatus as figured above, which is said to effect a marked economy in operation.

The standard types of apparatus and (when working a nine-tenths per cent brine) guaranteed production are given as follows:

Type	Volt	Amps.	Kilo-watts	Kgs Cl per hour	Kgs Cl in 22 hours
E K 110-120	110	120	13.2	1.50	33
E K 110-60	110	60	6.6	0.75	16.5
E K 110-30	110	30	3.3	0.40	8.8
E K 110-15	110	15	1.6	0.20	4.4
E K 60-120	60	120	7.2	0.80	17.6
E K 60-60	60	60	3.6	0.40	8.8

This system is in use in a considerable number of bleacheries, laundries and pulp and paper mills in Europe, a large installation being at the works of the Kellner-Partington Paper Co. in Austria.

Another method for producing bleaching liquor, much used on the Continent, is that known as the Schuckert system. The latest form of this apparatus is manufactured by the Siemens-Halske Co., of Berlin, and is shown in Fig. 8. The electrolyzers are large troughs of stoneware or other resistant material separated into eight or ten compartments. In these compartments are bipolar electrodes of peculiar construction, in which platinum-iridium wire may or may not be used. The brine enters one end and traverses the cell in a zigzag fashion, being constantly mixed by the escaping hydrogen gas. No pump or other external means of insuring circulation is employed. Each cell is provided with a cooling coil through which a stream of water is maintained. The units are built in pairs and are designed to be used on a 110-volt circuit. The standard types of apparatus with the output of each, is given as:

Type	Kg active chlorine in 10 hours	Liters of bleaching solution	Amperes at 110 volts
P 35	4-45	225	35
P 50	6-65	340	50
P 75	10	500	75
P100	13	650	100
P125	16	800	125
P150	20	1000	150

The relation between concentration of active chlorine and the energy and salt consumed is shown by the following data:

A 10 per cent salt solution in traversing a pair of electrolyzers may have according to its speed a final content of chlorine.

Grams per liter	Energy consumed in kw per 1 kg chlorine	Salt used in kilos per 1 kg chlorine
20-22	7	5- 5.3
16	6	6- 6.5
10-12	5	10-10.6

By using a 15 per cent brine the energy is reduced and the salt consumption increased as follow:

Grams Cl per liter	Energy in kw	Salt in kilos
20-22	5.5-6	7.5- 8
10-12	4.5-5	15-16

With a 20 per cent salt solution a concentration of 45 grams per liter may be obtained, although in this case the current efficiency falls to 45 per cent. It has in general been found advisable to produce a solution containing 20 grams of active chlorine per liter and to later dilute with water to the desired strength. In the accompanying Fig. 1 is seen a plant located at Billingsfors, Sweden, which supplies the liquor necessary to bleach 16 tons of soda spruce cellulose per day. By the Siemens-Schuckert Co. is controlled the patent already referred to for the use of sodium resinate ("resin soap") in reducing the destructive action of hydrogen on the hypochlorite. The thin film of colophonium doubtless acts as a continuously forming and evidently an efficient diaphragm.

The third system which has become prominent in Europe is that of Haas and Oettel. The electrolyzers are built and sold by Haas and Stahl, Aue in Saxony. The earlier forms were intended for bleacheries and laundries, and an apparatus complete with the necessary reservoir for brine and storage tank for finished bleaching liquor is shown in Fig. 6.

The electrolyzer proper consists in a small rectangular box of a resistant tar or asphalt composition, divided into small

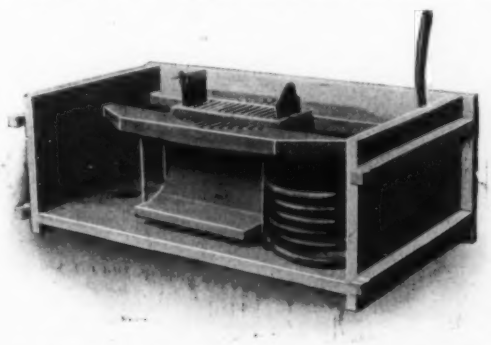


FIG. 7.—LATEST FORM OF HAAS AND OETTEL APPARATUS.

compartments by a series of vertical bipolar carbon electrides, set in insulated grooves. A 4B° salt solution passes through oblique perforations in the electrode, which are out of alignment, and receives more or less of a whirling motion, which aids in its thorough mixing. It issues from the lower end of the electrolyzer as liquor containing about 3 grams of active chlorine per liter.

A later modification capable of yielding liquor carrying 20

grams of available chlorine per liter is shown in Fig. 7. The electrolyzer itself is placed in a large wooden box, which is to hold the salt solution to be decomposed. At the bottom of each small compartment are two holes, opening to either side of the electrolyzer at its lower edge. The top of each compartment overflows into a canal which empties at one end of a side piece running the length of the box. When the current is turned on hydrogen is set free in each compartment and mixing with the brine raises the specific gravity of the mass to such an extent that the liquor within the cells fails to balance that on the outside. As a result a current is set up in the liquor, the brine in the tank passing into the apparatus through the holes at the bottom and overflowing through the canals which empty at the corners of the box. A cooling coil is provided by which the temperature is kept below 24° C.

On account of the absence of platinum this type of apparatus is comparatively cheap. Each unit is designed to take about 75 amperes from an ordinary lighting circuit. In a salt solution of from 4 to 6B° one kilo of active chlorine may be produced by the expenditure of energy equivalent to about 6½ hp-hours.

It was the pleasure of the writer to see two of the above units in operation at the cotton mills of Wolle & Co., at Aue. Each electrolyzer sat in a wooden tank holding 1000 liters of 12 per cent brine. The circulation of the liquor through the tank and electrolyzer seemed to be all that could be desired, the operation progressing without attention and without any appreciable odor of chlorine. The content of active chlorine in the liquor is brought up to 15 grams per liter in the electrolyzers, and when ready for use is diluted to about 3 grams per liter. The cotton cloth is drawn through the solution, pressed lightly between rolls and allowed to stand for three or four hours in the air. A high color is in this way produced and the goods are then soured in a very dilute acid and washed. The specially prepared carbons in use were said to have been in active service for one and one-third years, the plant bleaching from 15,000 to 20,000 pounds of cotton daily; they showed however, little sign of disintegration or wear. A large number of plants have been equipped with the apparatus, one of 120 hp being for the North German Lloyd Steamship Co., at Bremen. Here all the linen from the company's many ships is washed and bleached. Although the principle on which the bleaching action of all hypochlorites depends is the same, experience has shown that for equal concentration of active chlorine, as shown by analysis, that held as sodium hypochlorite produced electrolytically, is much the more powerful in its action. This difference in the bleaching power varies with the material acted upon, but on the average lies between the ratios 3:2 and 5:4. This is doubtless due to a more efficient use of the available chlorine brought about in part by the absence of free alkali in its solution, which renders possible the presence of a greater amount of free hypochlorous acid and also in part by the greater solubility and rate of diffusion of the sodium salts as compared with calcium salts.

Unquestionably there are in the use of electrolytically prepared bleaching liquors advantages not possessed by those made from chloride of lime. The color of the finished goods is purer and more even; the solution penetrates the fibres more easily, giving a color of greater permanence; there is no danger of the deposition of insoluble calcium salts producing a harsh or rough feel on the goods. The cost of plant, especially where carbon electrodes are used, is not great when compared with our diaphragm cells, and the labor of repair and operation is much less. For laundries, bleacheries and textile works generally processes of the kind above-mentioned deserve more attention from Americans than they have as yet received. For our large pulp and paper mills, especially those in which caustic soda is used to reduce the wood to fibre, the diaphragm cells seem to have the advantage. For, leaving out of consideration the somewhat increased consumption of power and salt, the fact remains that in the systems for the direct production of bleaching liquor we are using the relatively expensive caustic soda, when the cheap caustic lime may be employed.

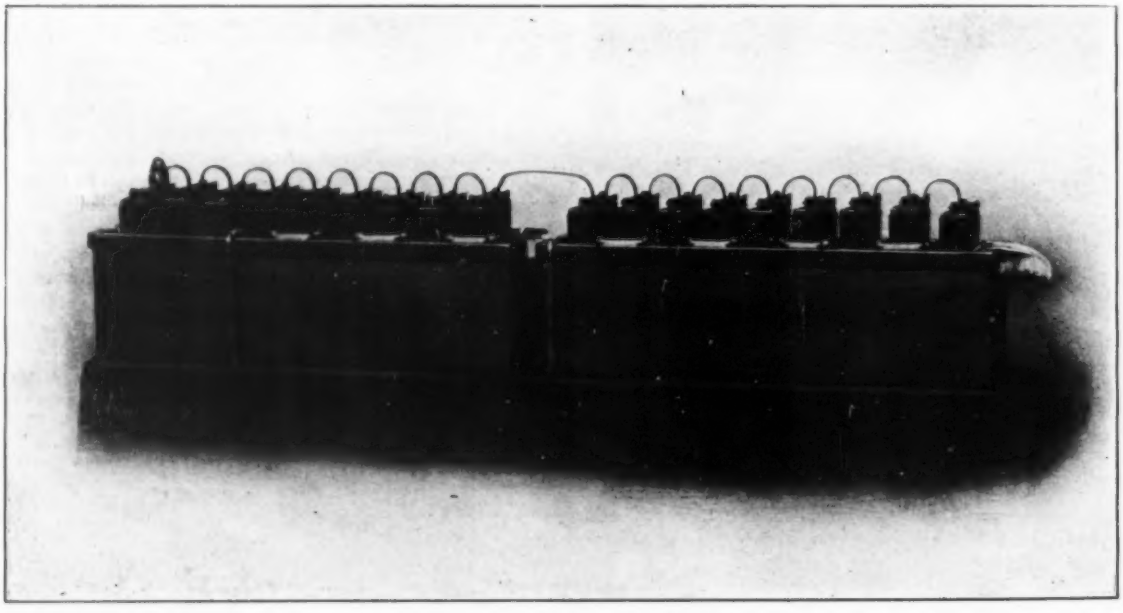


FIG. 8.—SCHUCKERT APPARATUS.

JOURNAL DE CHIMIE PHYSIQUE.

While Germany has Ostwald's *Zeitschrift f. Physikalische Chemie*, and the United States Bancroft's *Journal of Physical Chemistry*, no journal specially devoted to physical chemistry was published up to the present in the French language. To fill this need, the *Journal de Chimie Physique* has just been founded. It is to appear as a monthly. Prof. Phil. H. Guye, of Geneva, Switzerland, is editor. We wish every success to our new contemporary.

ELECTROLYSIS AT SMOOTH AND PLATINIZED PLATINUM ANODES.

BY PROF. F. FOERSTER, PH. D.

DIFFERENCE IN THE BEHAVIOR OF SMOOTH AND PLATINIZED ANODES AT WHICH NO OXYGEN IS EVOLVED.

If an electric current of any strength shall enter an electrolyte through an inert anode, the latter must be at a potential which is sufficient in the electrolyte to enable that chemical reaction to take place which requires the least amount of chemical work at this electrode. This work is generally determined by the potential which the substance to be separated impresses in its turn on an electrode which dips into the same electrolyte.

To explain this statement by an example, we may discuss the electrolysis of a neutral normal solution of potassium iodide. The current will perform here at a platinum anode the separation of iodine, as this requires the least amount of work, and the iodine will soon saturate the solution in the immediate neighborhood of the anode. The potential, which the anode must have in order to enable this reaction to take place, is the same as that of a sheet of platinum in a normal solution of potassium iodide saturated with iodine. This is according to the formula of Nernst:

$$e = \frac{0.002\,T}{2} \log k \frac{C_{I_2}}{(C_{I'})^2}$$

in which T is the absolute temperature, C_{I_2} the concentration of free iodine, $C_{I'}$ the concentration of the iodine ions at the anode, and k a constant. The value of e in this case equals—0.56 volt against the normal hydrogen electrode.

If the electrolysis is carried out with a comparatively high anodic current density, more iodine ions will be discharged at the anode than can be brought back by diffusion to the anode in the same time. The concentration of the iodine ions will, therefore, become smaller near the anode than in the rest of the electrolyte, and the anode potential must increase. But with increasing difference of concentration between the neighborhood of the anode and the rest of the solution, the velocity of diffusion towards the anode increases, and, on account of the change in specific gravity, the impoverished solution is also carried away from the anode by convection; a condition will, therefore, soon be reached, when no further decrease of the number of iodine ions at the anode occurs, compared with the rest of the electrolyte, and, therefore, the anodic potential becomes constant. The value reached in this way, depends mainly on the current density.

It is thus clear that it is of importance whether the electrode, from which a certain current of a certain intensity enters the electrolyte, is smooth or rough. In the latter case the surface of the electrode is increased, the current density, therefore, decreases, and, what may be of still greater importance, the electrode reaches with its higher points further into fluid-strata, in which, when the electrolyte near the deeper points of the electrode is strongly impoverished, a part of the electrolytic action may take place, until the impoverishment has been somewhat relieved.

A rough anode of considerable active surface is obtained by coating a sheet of platinum with platinum black. If the platinizing is done with a pure solution of hydrochloroplatinic acid, there is obtained in most cases a coating of gray platinum sponge, which has little effect. In order to be sure to obtain a deep black coating of platinum, according to Lummer and Kurlbaum[1] 0.025 gram of crystallized lead acetate is added to a solution of about 1 gram of platinum in 100 cc, and the sheets of platinum are platinized in this solution with a current density of 0.03 amp. per square centimeter for 1 to 2 minutes.

The influence of platinizing on the anode potential cannot be very considerable; this is shown by the above formula of Nernst. From this we see that, for instance, a diminution of $C_{I'}$ to one-tenth of its value at ordinary temperature (17° C.) would raise the anode potential by 0.058 volt only. An impoverishment of the ions to be discharged to much less than say 1/100 of the initial value is, however, scarcely probable.

In agreement with this theoretical result is the observation[2] that in the electrolysis of an alkaline potassium iodide solution at a given constant current strength, the voltage is increased only by 0.07 volt, if the platinized anode is replaced by a smooth one. F. Salzer[3] made a similar observation when he electrolyzed an oxalic acid solution with a small current density; under these circumstances it is oxidized at the anode to carbonic acid with a current efficiency of 100 per cent.; the substitution of a smooth anode for the platinized one, everything else being the same, caused an increase of potential by 0.12 to 0.21 volt only. The difference is greater here than in the case of the potassium iodide, because the smooth anode covers itself with large bubbles of carbonic acid, which adhere to it for quite a while and render the approach of the electrolyte to the electrode very difficult.

While in these observations which are in satisfactory agreement with the theory, the differences between the potential required for rough and for smooth anodes are small, considerably greater differences are observed, when hydrogen, and especially oxygen, are developed at the electrodes.

THE POTENTIAL REQUIRED FOR THE BEGINNING OF THE ELECTROLYTIC GENERATION OF OXYGEN.

Poggendorff[4] found as far back as 1847 that for the electrolysis of a solution of sulphuric acid a considerably greater voltage is required between smooth platinum electrodes than between platinized ones. In the first case, as was established more accurately later on by Fromme,[5] there is required a voltage of 2.5 to 3.0 between the electrodes, while in the latter case only 1.8 to 1.9 volts are necessary under the same experimental conditions.

The question now arises whether the generation of hydrogen at the cathode, or that of oxygen at the anode, or both, cause this extraordinary increase of e. m. f. The facts show that the latter is the case. It is well known[7] that the first bubbles of hydrogen appear at a rough cathode always at a somewhat lower cathode potential, than at a smooth cathode of the same material. It has not yet been systematically investigated how large the increase of potential will be with a somewhat greater current strength. But it is known[7] that, for instance, the cathode potential required for the generation of hydrogen from sulphuric acid is greater by about 0.25 volt at a spongy lead plate than at a smooth lead plate.

The anodic potential, required for the anodic generation of oxygen, has been more thoroughly examined of late. The potential, which is impressed by oxygen of atmospheric pressure on a platinized electrode dipping into sulphuric acid of normal H concentration is about 1.13 volt against the normal hydrogen electrode,[8] and the same difference of potential is shown by a hydrogen-oxygen gas cell in caustic alkali. If one impresses, however, on a small metallic electrode a potential different by 1.12 to 1.13 volts from that which hydrogen possesses against the same solution, then a small current begins to pass through the electrolyte and hydrogen appears at the cathode, but it does not come to a generation of oxygen gas at the anode; there is formed instead in the solution an oxydizing agent whose nature is still unknown and which is likely to be the source of the peroxide of hydrogen appearing at the cathode. For the generation of gaseous oxygen which is coincident with the passage of a stronger current, a considerable increase of the anode potential above 1.13 volt is necessary, and, as has been shown by the very interesting ex-

[1] See Kohlrausch, Wiedemann's Annalen, v. 60, p. 315.

[2] Forester and Mueller, Zeitsch. f. Electrochemie, v. 8, p. 534.
[3] Zeitsch. f. Electrochemie, v. 8, p. 898.
[4] Pogg. Ann., v. 70, p. 177.
[5] Wiedem. Ann., v. 38, p. 362.
[6] E. Mueller, Zeit. f. Anorgan. Chem., v. 26, p. 1.
[7] Strasser and Gahl, Zeitsch. f. Electroch., v. 7, p. 11.
[8] Bose, Zeitsch. f. Electrochemie, v. 7, 673.

periments of Coehn and Osaka,[9] this potential depends on the nature and the condition of the surface of the anode. It has been found that the following potentials must be impressed on an anode in caustic potash against a hydrogen electrode in the same solution, in order to enforce the passage of a strong current with generation of oxygen:

At spongy nickel	1.28	volts
At smooth nickel or cobalt	1.35	"
At iron	1.47	"
At platinized platinum	1.47	"
At smooth platinum	1.67	"
At gold	1.75	"

In future it will be very interesting to examine by experiment the conclusions which may be drawn from these facts, and which are theoretically and practically of equal importance.

The above values only relate to such very small currents as flow when the e. m. f. between the electrodes is just a little above the voltage of decomposition. Concerning other points of the behavior of anodes at which oxygen is generated, we have a more definite knowledge only in the case of the two kinds of platinum anodes. The investigations on this point, which I have carried out together with my colleague, Dr. Erich Mueller,[10] in the electrochemical laboratory of Dresden, and which were continued by other gentlemen experimenting there, have shown that there are other differences in the electrochemical behavior of both kinds of electrodes, besides the overvoltage (Ueberspannung) required for the generation of oxygen at smooth platinum over that required at platinized platinum, as indicated in the above table.

ON THE POTENTIAL OF SMOOTH AND PLATINIZED PLATINUM ANODES AT WHICH OXYGEN IS GENERATED.

It is possible to obtain by the following simple means an idea of the changes which the potential of an anode at which oxygen is generated undergoes during the passage of the current.

If we electrolyze an electrolyte which gives oxygen at the anode—like sulphuric acid or caustic soda—with two vertical platinized platinum cathodes, while the platinum anode suspended between them is either smooth or platinized, we notice that the voltage at the terminals of cell increases while electrolysis is going on. Special experiments have shown that for a given current strength the potential of the platinized cathode remains quite constant for many hours. Moreover, by carefully keeping the current strength and the temperature of the electrolyte constant, it is possible to exclude any change of the e. m. f. due to a change of resistance of the electrolyte. Hence the change of the voltage at the terminals of the cell, which is observed under such experimental conditions, must be due to a change of the anode potential. If for measurements of the voltage a very well damped voltmeter of large internal resistance is used it is possible to measure with sufficient accuracy the difference of potential which the platinized anodes have against the cathodes charged with hydrogen, immediately after interruption of the current. The value of the counter electromotive force thus found will be called p in the following. For smooth anodes the same determination cannot be carried out with certainty on account of their very small capacity.

Table 1 gives the results of experiments, which show the course of the phenomena more in detail. The current strength was 0.5 amp., which is equivalent to a current density of 0.017 amp. per sq. cm; the temperature was kept at 10° C.

The results of these experiments are also represented by the curves in figure 1, in which the drawn-out lines relate to platinized anodes, and the dotted lines to smooth anodes.

According to these experiments, platinum anodes at which oxygen is developed show special peculiarities in two directions. First, we see that their potential increases considerably during the course of electrolysis. Second, we see that smooth platinum anodes assume a much higher potential than platinized anodes. In the following these two sides of the phenomenon will be scrutinized somewhat more closely.

THE INCREASE OF THE POTENTIAL AT ANODES AT WHICH OXYGEN IS DEVELOPED.

At a *platinized* anode the potential increases first quickly, then more slowly, but even after considerable lapse of time this increase does not stop completely. The potential thereby reaches values which are about 0.4 volt above that at the beginning of the experiment.

This increase of potential cannot be caused by a gradual impoverishment of the anions required for discharge, because the change of concentration which occurs until a stationary condition is reached, and which depends on the current strength used, requires only a fraction of a minute to become complete at electrodes at which no oxygen is developed, as, for instance, in the electrolysis of potassium iodide, and then the anodic potential remains quite constant for a considerable

[9] Zeitsch. f. Inorgan. Chemie., v. 3, 4, 86.
[10] Zeitsch. f. Electrochem., v. 8, p. 515.

TABLE I.

Experiment 1.			Experiment 2.		Experiment 3.			Experiment 4.	
Electrolyte 2n. H_2SO_4.					Electrolyte 2n. Na O H.				
Platinized Anode.			Smooth Anode.		Platinized Anode.			Smooth Anode.	
Time After the Beginning of the Experiment.	Voltage at the Terminals.	P in Volts.	Time After the Beginning of the Experiment.	Voltage at the Terminals.	Time After the Beginning of the Equipment..	Voltage at the Terminals.	P in Volts.	Time After the Beginning of the Experiment.	Voltage at the Term'ls.
Immediately after closing of the circuit.	1.7	.....	Immediately after closing of the circuit.	2.27	Immediately after closing of the circuit.	1.8	----	Immediately after closing of the circuit.	2.20
½ minute	1.79	----	½ minute	2.28	½ minute	1.84	----	1 minute	2.41
1 "	1.80	----	1 "	2.30	1 "	1.855	----	2 "	2.49
2 "	1.82	----	2 "	2.31	2½ "	1.88	----	3 "	2.57
3 "	1.84	----	6 "	2.33	4 "	1.89	----	4 "	62 3
4 "	1.85	----	10 "	2.34	6 "	1.91	----	6 "	2.72
5 "	1.86	----	23 "	2.35	10 "	1.94	----	10 "	2.77
15 "	1.91	----	33 "	2.36	25 "	1.99	----	30 "	2.88
30 "	1.94	----	53 "	2.37	30 "	2.01	----	60 "	2.92
59 "	1.95	1.74	80 "	2.39	50 "	2.04	----	75 "	2.93
70 "	1.99	1.78	2 hours	2.40	60 "	3.05	----	2 hours	2.91
2 hours	2.02	----	4 "	2.41	80 "	2.07	1.84	3 "	2.90
4 "	2.06	1.84	5 "	2.42	4 hours	2.13	1.90	6 "	2.90
6 "	2.07	----	6 "	2.41	6 "	2.15	----	7 "	2.23
7 "	2.07	----	7 "	2.41	21½ "	2.225	1.98	21 "	2.89
8 "	2.075	----	8 "	2.415	25½ "	5.23	----	----------	----
22 "	2.107	----	22½ "	2.415	50 "	2.255	2.0	----------	----
26 "	2.11	----	----------	----					
33 "	2.115	----	----------	----					
46 "	2.120	1.90	----------	----					

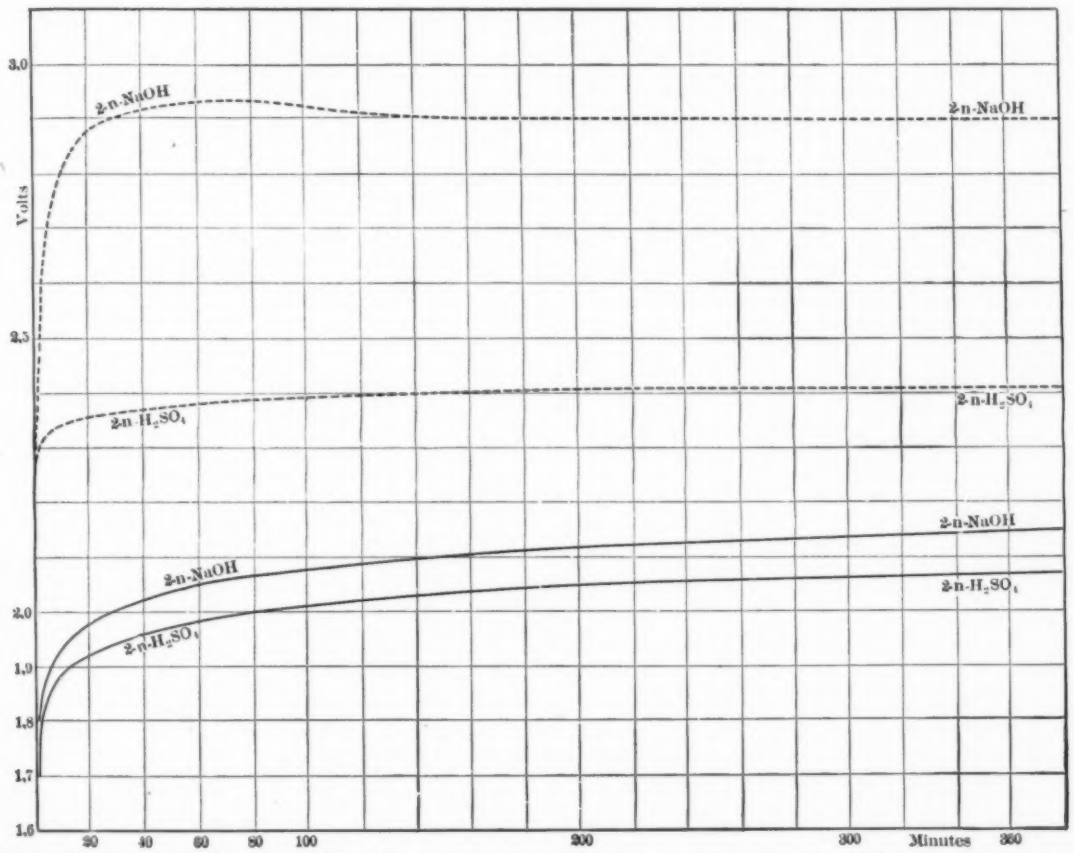
time. The fact proven by these experiments, that the development of oxygen at a platinized anode requires an increasing amount of work while electrolysis is going on, must be attributed to a gradually increasing change *in* the platinized electrode.

The following observations confirm this: If the current is interrupted after electrolysis has been carried on for some time, and if the circuit is closed again a few seconds later, electrolysis commences at the same potential at which it had stopped; and even, after an interruption of several minutes, when the circuit is closed again, the potential is only a little below the former one, and this is soon reached again. One may even take an electrode which is polarized to a high anodic potential, out of the electrolysis and wash it off, to use it again as an anode in another solution; when electrolysis is then started in the new solution the anodic potential is a few tenths of a volt higher than would be the case if a freshly platinized anode had been used. But if an anodically polarized electrode is used as cathode until hydrogen is generated at it, and is then made again anode, it acts like a freshly platinized plate.

Therefore, we may imagine that during electrolysis small parts of the anodically generated oxygen are absorbed by the platinum black and are stored in it at a gradually increasing pressure. After the external force has ceased, this oxygen is only slowly given off again. The condition in which the oxygen is stored in the platinum black is not necessarily that of a simple gaseous solution; such a solution would have to be assumed to be under enormous pressures. It is very well possible that we have here a platinum-oxygen compound, which, however, must then be assumed to be dissolved in platinum black in steadily varying concentration; this assumption is necessary in view of the *steady* increase and decrease of the potential.

Remarkable is the following fact which shows that only a small quantity of oxygen can be present in the platinum black. The increase of potential of a platinized anode in caustic soda solution takes place in an almost unchanged manner, if, for example, by means of addition of sodium formate 90 per cent. of the anodic oxygen are prevented from being liberated and are used for oxidizing purposes. If, on the other hand, the anodic potential is kept at a value not sufficient for the development of any oxygen, by means of a suitable depolariser, as, for instance, concentrated oxalic acid solution, then the potential does not change even by 0.01 volt in one hour.[11]

The temperature has a material influence on the increase of the potential of a platinized anode at which oxygen is developed. The lower the temperature, the greater is the increase of the anode potential in the course of time. Under otherwise the same conditions as in experiment 3 of the above table, but at a temperature of 75° C., the anodic potential was found to rise by 0.13 volt in the first two hours, and then to remain constant; therefore, the increase of potential was only one-third of that which took place at 10°.[12]



CURVES OF THE POTENTIAL OF SMOOTH AND PLATINIZED PLATINUM ANODES AT WHICH OXYGEN IS DEVELOPED.

At a *smooth* anode the anodic potential also arises quite considerably during the course of electrolysis. This increase, however, takes place much more quickly than at a platinized anode, and the anodic potential soon assumes a value which remains constant for a long time. But if the current is now interrupted and closed again right away, the voltage at the terminals of the cell is near its initial value, and about the same time, as before, must elapse before the voltage reaches

[11] F. Salzer, Zeit. f. Elektrochemie, v. 8, p. 898.
[12] Foerster and Mueller, Zeit. f. Elektrochemie, v. 9, p. 205.

again the value observed before interruption of the current. Whether this fact is solely due to the very small capacity of smooth platinum anodes as compared with platinized anodes, or whether there are special phenomena taking place here besides those which cause an increase of potential at platinized anodes, is still an open question.

THE DIFFERENCE BETWEEN THE POTENTIALS OF PLATINIZED AND SMOOTH PLATINUM ANODES WITH OXYGEN DEVELOPMENT.

Of considerable importance is the second property of platinum anodes at which oxygen is developed, namely, that for the same strength of current the voltage drop at a smooth anode is much greater than at a platinized anode. The difference between the potentials which both kinds of anodes assume in the above-mentioned experiments increases at the beginning to very considerable values. These, however, become later somewhat smaller, when during the course of electrolysis the potential of the platinized anode approaches its maximum value. This difference between the potentials of both kinds of anodes was found to have the following values: At a current density of 0.017 amp. per sq. cm, after 10 to 11 amp.-hours it was

in 2n H_2SO_4 0.308 volt,
in 2n NaOH 0.665 volt;

at a current density of 0.067 amp. per sq. cm, after 8 amp.-hours it was

in 2n H_2SO_4 0.46 volt,
in 2n NaOH 0.75 volt.

The difference between the potentials depends, therefore, upon the nature of the electrolyte and the current density; and an increase in temperature seems to decrease it. It is seen that this difference in potential is considerably larger than 0.2 volt, which is the difference between the potentials required for the beginning of the generation of oxygen at platinized and smooth platinum anodes and must, therefore, not be identified with it, although it is probable that the same or similar causes are at the bottom of both facts. What these causes are cannot yet be stated. We can only assert that it is probable that the difference of the work necessary for the formation of gas bubbles as smooth and at rough surfaces can only, to a small degree, cause the large excess of the voltage required for developing oxygen at a smooth anode over that required at a rough anode.

The question of the nature of this strong increase in potential at a smooth platinum anode becomes of special interest if it is formulated as follows: When oxygen is developed at a smooth platinum anode, is it necessary to overcome a considerable transition resistance at the electrode so that the surplus of voltage consumed corresponds merely to a development of heat, or is it wholly or partly available for performing chemical work?

That the latter is the case, might be concluded from the fact that quite a number of anodic reactions are dependent upon the presence of smooth platinum electrodes, and either do not take place at all or with a very small current efficiency at platinized electrodes. Such processes are, for instance, the formation of persulphuric acid and its salts, the formation of ethane in the electrolysis of acetates or the electrolytic production of perchlorates. All these are reactions which go on well if carried out with a high anodic current density and a high concentration of certain anions, whose discharge is essential for the reaction:[12]

$$2\,HSO'_4 + 2\,F = H_2S_2O_8$$
$$2\,CH_3CO'_2 + 2\,F = C_2H_6 + 2\,CO_2$$
$$\left.\begin{array}{r} 2\,ClO'_3 + H_2O + 2\,F = ClO'_4 + ClO'_2 + 2\,H^{\cdot} + O \\ ClO'_2 \quad O = ClO'_3 \end{array}\right\}$$

Lately it has been made probable through experiments by W. Oechsli in the Dresden laboratory that the mechanism of the electrolytic formation of perchlorate is expressed by the latter equations.

It requires, however, generally much more work to discharge acid anions containing oxygen than OH′ ions, and this is probably also true when they are present in such a small concentration as in water. At smooth anodes the reactions take place in a very small space, and the concentration of the OH′ ions will be very quickly diminished by the acidification accompanying the discharge of the anions, so that the current then depends on the discharge of the other anions. On the other hand, at a platinized anode such a strong diminution of the concentration of the OH′ ions will not take place at all, and the discharge of acid anions will occur to a small degree only or not at all. It is possible to obtain the same result at a smooth anode by adding a small amount of alkali to the solution; and, in fact, from the experiments made with the three reactions mentioned above, it is possible to state, as a rule, that an anodic process which gains considerable extent only at smooth but not at platinized platinum anodes, can be wholly or partly suppressed at a smooth anode if a small quantity of alkali is added to the electrolyte. In the latter case there is not the same diminution of anode potential as with platinized anodes; therefore, the phenomena in question cannot altogether be assumed to be due to the higher potential at the smooth platinum anode. For the explanation of the influence of smooth platinum anodes on those phenomena, it is sufficient to assume that there is a much smaller OH′ concentration and a larger concentration of acid anions at smooth than at platinized anodes; hence this is an analogy to the difference above mentioned in the electrolysis of potassium iodide with smooth and with platinized anodes, and it still remains to be decided whether special electrochemical processes may be caused by the specially high potential at a smooth platinum anode.

The above described behavior of platinum anodes at which oxygen is developed has already been found to be capable of practical application for various purposes. A few examples may be given.

ALKALI CHLORIDE ELECTROLYSIS WITH SMOOTH AND PLATINIZED PLATINUM ANODES.

If neutral strong alkali chloride solutions are electrolyzed for manufacturing hypochlorites and chlorates, and if the anode is platinized, nearly chlorine ions alone are discharged at it, with a current efficiency of about 99 per cent. besides very small quantities of oxygen. The anodic potential is determined by the separation of chlorine, and reaches very soon a constant value which depends on the current density.[14] The chlorine developed at the anode reacts in the electrolyte with the hydroxide coming from the cathode, and the formation of hypochlorite results. When the ClO anions, thereby produced in the electrolyte, have reached a certain concentration in processes. They are thereby discharged, and react according to equation:[15]

$$6\,ClO' + 3\,H_2O + 6\,F = 6\,H^{\cdot} + 2\,ClO'_3 + 4\,Cl' + 3\,O.$$

So that chlorate is formed in the solution and oxygen is developed at the anode.[16] The oxygen development quickly becomes more brisk and soon reaches a value corresponding to about one-third of the current strength. In spite of this, however, the anodic potential does not rise; only at a high current density it rises very little.

This fact is very remarkable. The free hypochlorous acid, which was already present at the anode, besides chlorine, is a strong oxidizing agent, so that before oxygen escapes freely, the hypochlorous acid has already produced a certain oxygen pressure in the anode. For, according to Nernst, an oxidizing agent impresses its oxidation potential on the anode by producing in or on it an oxygen pressure corresponding to its nature.

[12] In these equations and those which follow later in this article, F. (abbreviation of Faraday) represents the electric charge of a positive monovalent gramion, about 96,600 coulombs.

[14] Foerster and Mueller, Zeit. f. Elektrochemie, v. 8, pp. 520 and 525.
[15] Concerning the meaning of F., see the foot note 13.
[16] Foerster and Mueller, Zeit. f. Elektrochemie, v. 8, p. 667.

In the present case, the anode potential, while determined in the first line by chlorine development, has a value sufficient for the development of oxygen, if, besides the Cl′ ions, a sufficient number of OH′ or ClO′ ions can reach the anode. Should the anode potential increase, due to the development of oxygen, then if solution and electrode shall continue to be in equilibrium, it would be necessary that the potential of the hypochlorous acid, *i. e.*, its concentration at the anode, also increases. But this acid is the less stable, the higher its concentration, hence a considerable increase of concentration is impossible. It seems that in this way the oxygen is prevented from increasing the anode potential in the otherwise usual manner.

If, however, the electrolysis is carried out with a *smooth* anode, say with a current density of 0.067 amp. per sq. cm, the anodic potential, which remains constant during the first minutes, is only about 0.12 volt above that observed at a platinized anode, that is about as much as is due to the greater impoverishment of chlorine ions, which takes place at a smooth anode. But the potential of chlorine against very dilute chloride solutions is very nearly equal to the anodic potential required for the development of oxygen from a weak acid solution (as which we may consider an aqueous solution containing free gaseous chlorine on account of the equilibrium $Cl_2 + H_2O = H^{\cdot} + Cl' + HOCl$). Therefore, as soon as the dilution of the chlorine ions at the anode has reached a certain degree, oxygen also appears, probably first by the discharge of the OH′ ions of the water, but very soon also by the discharge of ClO′ ions. It has been shown by Lorenz and Wehrlin[17] that this development of oxygen raises the anodic potential very soon considerably above its initial value, and, if compared with the platinized anode, it causes again an increase of potential of about the value determined above for caustic soda. For saturated sodium chloride solution at 10° it was found to be at a current density of 0.067 amp. per sq. cm. after 10 amp.-hours 0.82 volt, and a current density of 0.017 amp. per sq. cm after 11 amp.-hours 0.75 volt. In this case there is no equilibrium between the oxidation potential of the solution and the oxygen present in the electrode. One might conclude that a direct contact of the solution with the electrode is prevented by an intermediate layer of oxygen, and that it is its resistance which causes the great voltage loss at smooth anodes at which oxygen is developed.

In spite of the great difference in anodic potential, the replacement of a platinized anode by a smooth one does not produce any other essential change in the course of the electrolysis of alkali solutions. Especially the yield of chlorate per ampere hour at a platinized and smooth anode is the same as long as the electrolyte remains neutral, if the cathodic reduction of the hypochlorite is made imposible, according to E. Mueller's method,[18] by adding a small amount of chromate to the electrolyte. The formation of hypochlorite, produced by the current in the solution during the first part of the electrolysis, takes place with somewhat lower ampere-hour efficiency, and in a somewhat smaller concentration at a smooth anode than at a platinized anode, on account of the very early development of oxygen at a smooth anode; at a platinized anode a solution of 45 g bleaching chlorine was obtained in 1 liter. If, however, the watt-hour efficiency of the formation of chlorate at both kinds of electrodes is compared, it is at the smooth anode only 75 per cent. of that at the platinized anode.

The latter has still another special advantage, if a slightly acidulated chloride solution is used. As mentioned above, when a platinized anode is used, the concentration of hypochlorite can become pretty high in the electrolyte, without any discharge of ClO′ ions, which takes place with generation of oxygen and with diminished current efficiency. If at this stage of the process so much hydrochloric acid is added to the electrolyte, that hypochlorous acid can be formed only from a part of the hypochlorite, then we have in the electrolyte the conditions which are most favorable for the formation of chlorate. This takes place according to the reactions:[19]

$$2HOCl + NaClO = NaClO_3 + 2HCl;$$
$$2HCl + 2NaClO = 2NaCl + 2HClO; \text{ etc.}$$

By this secondary formation of chlorate in the acidulated electrolyte, the hypochlorite produced by the current can be continually used up before it reaches the concentration required for the discharge of its anions. In this case the production of chlorate in the electrolysis of alkali chloride solutions takes place with an ampere-hour efficiency of about 98 per cent. and an energy yield of 1 gram chlorate oxygen per 12.5 watt-hours at a current density of 0.117 ampere per sq. cm.[20]

At smooth anodes the development of oxygen reaches a considerable extent with a concentration of hypochlorite in the solution, at which the secondary formation of chlorate does not take place with sufficient velocity to change the hypochlorite produced by the current into chlorate as quickly as it is formed. Until this point is reached, the anodic generation of oxygen already amounts to about 12 per cent. so that the ampere-hour efficiency of the formation of chlorate at smooth anodes cannot be increased much above 88 to 89 per cent.

The conditions at a platinized anode represent nearly the ideal conditions for alkali chloride electrolysis. Whether this method of working can be used without modification in practice on a large scale, or whether it will only be possible to try and come as near as possible to these results in another way, must be left undecided. Under all circumstances it has to be remembered that platinized anodes can only find practical application in the electrolysis of *sodium* chloride solutions; for the chlorate, which crystallizes from *potassium* chloride dilutions, covers the platinized anode with a diaphragm, which offers a considerable resistance, and between this diaphragm and the anode a very dilute chloride solution is electrolyzed with a brisk generation of oxygen.

Theoretically important was the study of the course of electrolysis of strongly alkaline solutions of chlorides at a platinized anode.[21] Oettel[22] has shown in 1894 that such solutions behave in a peculiar manner at a smooth anode; he found that in the same the current forms at most only traces of hypochlorite, chlorate being already formed from the beginning of electrolysis. This phenomenon, which is so different from those observed in the electrolysis of a neutral solution, has given rise to many hypotheses.

If we consider that in a 1 normal alkaline 3 normal sodium chloride solution, only 0.87 volt is required at a smooth platinum anode for the generation of oxygen by OH′ discharge, but —1.35 volt for the generation of free chlorine, we should think that in a normal alkaline solution of a chloride it should be impossible to get a chloride electrolysis. If it occurs, nevertheless, the reason must be that in the course of the development of oxygen, the potential required for the further development of the gas undergoes a considerable increase.

In fact it was found that at a freshly-platinized anode in a normal alkaline solution of an alkali chloride, an electrolysis of chloride, as shown by the formation of oxygen-chlorine compounds, was hardly perceptible at the start. But when the anodic potential increases during the passage of the current, more and more chlorine is discharged, which is immediately used up for the formation of hypochlorite on account of the depolarizing action of the OH′ ions at the anode. Very soon the relatively low value of the potential[23] required for the discharge of ClO′ at the anode is passed, and these anions are discharged again immediately after their formation, and there-

[17]Zeitsch. f. Elektrochemie., v. 6, p. 437.
[18]Zeit. f. Elektrochemie, v. 5, p. 469, and v. 7, p. 398.
[19]Foerster and Jorre, Journ. f. pract. Ch., v. 59, p. 53, and v. 63, p. 141.
[20]Foerster and Mueller, Zeit. f. Elektrochemie, v. 8, p. 11.
[21]Foerster and Mueller, Zeit. f. Elektrochemie, v. 9, p. 200.
[22]Zeit. f. Elektrochemie, v. 1, p. 474.
[23]Foerster and Mueller, Zeit. f. Elektrochemie, v. 8, p. 634.

by form chlorate, as stated above. With continuing increase of potential, the current efficiency of the formation of chlorate increases. The only difference between these phenomena and those at a smooth anode is that at the latter the increase of potential takes place quickly, and the chlorate appears from the start nearly as the only product of electrolysis with a nearly constant efficiency from the first stage of the experiment.

Anyhow, it is also generated in this case by the anodic discharge of ClO' ions which have been primarily formed by the current, exactly as in a neutral solution. The apparently very great difference of both phenomena is that the beginning of the chlorate formation depends in a neutral solution upon the establishment of a certain concentration of ClO' ions in the *electrolyte*, while in an alkaline solution it depends upon the moment at which the *electrode* assumes a certain condition which determines the value of the anodic potential.

ELECTROLYSIS OF SODIUM SULPHITE WITH PLATINIZED ANODES.

The described phenomena at platinized anodes may be summed up in the statement that it is possible, to enable these electrodes by previous anodic polarisation to perform electrochemical work which they could not perform otherwise; one might say it is possible to train them. A further case, in which one can utilize this possibility, is found in the electrolysis of sodium sulphite.[24] This acts as a strong depolariser for oxygen; even at a comparatively high current density a solution of sodium sulphite may suppress any anodic generation of oxygen and may hold the anodic potential below the potential necessary for such generation.

In this case at a freshly-platinized anode the sulphite is quantitatively changed to sulphate, according to the equation.[25]

$$SO_3'' + 2OH' + 2\,F = SO_4'' + H_2O$$

But if one uses as anode a plate of peroxide of lead, which has a comparatively high anodic potential, then only about half of the current furnishes sulphate, while the other part furnishes sodium dithionate according to the equation.

$$2\,SO_3'' + 2\,F = S_2O_6''$$

The same effect as on a lead peroxide anode may be obtained on a platinized anode, if it is charged previously for some time anodically with oxygen in a caustic solution and is used immediately afterwards for the electrolysis of sulphite solution. In such a solution, containing 380 grams Na_2SO_3, $7H_2O$ in one liter, at a current density of 0.01 ampere per sq. cm. a freshly-platinized anode had the potential —0.32 to —0.35 volt against the normal hydrogen electrode, and at the same time sulphate was formed with 100 per cent. current efficiency. But when the same anode was used first as anode for 40 hours in a very pure caustic soda solution, and was then employed for the electrolysis of the sulphite solution, it showed, at a current density of 0.01 ampere per sq. cm., the potential of —0.64 to —0.78 volt and 47 per cent. of the current formed dithionate and 53 per cent. formed sulphate. By short cathodic polarization the electrode lost almost entirely the power to form dithionate.

USE OF PLATINIZED ANODES IN QUANTITATIVE ANALYSIS BY ELECTROLYSIS.

Another use of platinized electrodes, which has recently been developed by P. Denso,[26] refers to an essentially different field. The quantitative determination of copper by electrolysis would be most simple, if one would connect the poles of an accumulator directly to the binding posts of the platinum electrodes, which dip into the copper solution. Its e. m. f. of 2 volts is sufficient to deposit the copper quantitatively from a sulphate solution, while the separation of the metals Ni, Co, Fe, Cd, Zn, which so often accompany the copper, is thereby made impossible, and a quantitative separation of the copper from the latter might be obtained at the same time. As with such an arrangement only a small current passes through the electrolyte, the evolution of gas at the electrodes is so small that the electrolyte does not spatter or splash in such manner as to disturb the analysis, and the electrolysis does not need watching. The copper is deposited in bright red, dense form, without having nitric acid in the solution; at the end of the deposition of copper it is therefore possible to take the cathode out of the electrolyte, without having to fear any loss, and to wash the solution adhering to it back into the electrolyte, in order to determine another metal present in the electrolyte by electrolysis. For this purpose it is then only necessary to make such additions to the electrolyte as are required for the intended metal-deposition, and to use an e. m. f. higher than 2 volts.

While this extremely simple method of working has already been proposed by Freudenberg[27] ten years ago, it has up to the present not been introduced into analytical practice; the essential reason seems to have been that the current which passes through the electrolyte in this case drops very soon to such a small value that the determination of copper requires a comparatively very long time. It takes at least eight hours to deposit 4.25 grams of copper on a Winkler[28] wire gauze electrode against the usual spiral of smooth platinum wire with the current from one accumulator, and electrolysis is best carried out over night.

But as the voltage of decomposition of a normal copper sulphate solution is only 1.4 volts, and as the resistance of the solution can easily be reduced by sulphuric acid, it is somewhat difficult to perceive why, with this arrangement, only such a small current passes through the solution. The reason is that, on account of the impoverishment of copper near the cathode, and more especially on account of the increase of potential at the smooth anode, the polarization e. m. f. of the cell during the passage of the current is soon much nearer the value of 2.0 volts than the theoretical minimum of 1.4 volts.

The counter electromotive force of the cell is decreased and the current strength therefore increased, if a platinized anode is used. Moreover, if we fasten it to the clapper of an electric bell, which is arranged without the bell on the stand for electrolysis, we get at the same time a stirring device which diminishes the impoverishment of copper at the cathode and also contributes to an increase of current strength. It is thus possible to deposit with the current from one accumulator 0.1 gram of copper quantitatively in 1½ hours, and 0.25 grams in 3½ to 4 hours. The possibility is thus given to introduce this most simple and most rational method of quantitative determination of copper into practice.

CONCLUSION.

The investigation of the generation of oxygen at platinum anodes, which was apparently of theoretical value only, has thus already proven useful in several directions, and these researches may be expected to give still more useful results in future, when the electrolytic oxidation of organic compounds will be studied as closely as electrolytic reductions have been studied. The electrolytic oxygen which is developed at platinum, the material mostly used for anodes, possesses an extremely energetic oxidizing action. This is already shown by the fact that it often contains ozone. It is, therefore, capable of oxidizing completely organic bodies of high stability. For instance, pyridine is destroyed at a platinized anode, and this occurs the more rapidly the higher the potential becomes. A conclusion to be drawn from the theory which may at first sight sound paradoxical, but which is proven to be correct by experiment, is that at elevated temperatures when the increase of anodic potential is very much smaller than in the cold, the pyridine is less susceptible to electrolytic oxidation than in the cold. If one wants to use electrolytic methods for oxida-

[24] F. Foerster and A. Friessner, Ber. Deutsch. Chem. Ges., v. 35, p. 2514.
[25] Concerning the meaning of F., see foot note 13.
[26] Zeit. f. Elektrochemie, v. 9, p. 463.
[27] Zeit. f. Physik. Chem., v. 12, p. 97.
[28] Ber. Deutsch. Chem. Ges., v. 32, p. 2192.

tion purposes, it will be necessary to keep the potential necessary for the appearance of oxygen at a low value, if we have not to do with strongly depolarizing reducing agents which suppress the generation of oxygen completely.

As Coehn and Osaka emphasize, their observations, mentioned before, furnish pointers to perhaps valuable new methods, and the prospect becomes still brighter if the use of peroxide electrodes such as Ni_2O_3, Co_2O_3, Mno_2, Clo_2, etc., is taken into consideration. Here is still a wide field open for investigation which promises success.

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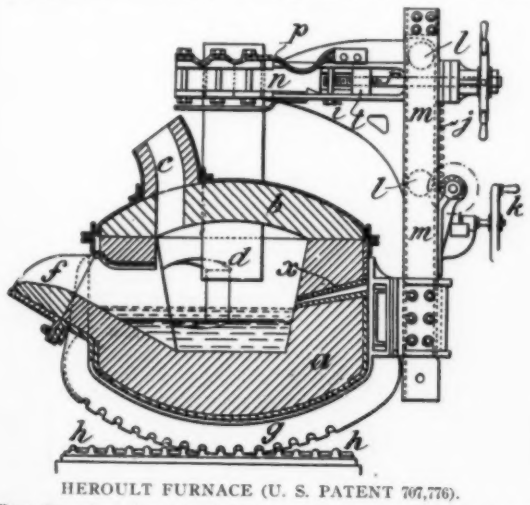
ELECTRIC STEEL PROCESS.

BY P. L. T. HEROULT.

In 1899 I was led to find out some process for making what is generally known as low-carbon ferro-chromium. After some unsuccessful experiments I came to the conclusion that the only way of manufacturing the above-named article was to do away with the usual form of electrical crucible. Therefore, having coupled two of my dynamos in series, I made a furnace in which the current jumped from the end of the electrode to the metal to be heated, in the usual form of an arc. But instead of leaving said metal through the bottom or sides of the crucible, it jumped again from the metal to the tip of another electrode, parallel to the first one. By this very simple arrangement the furnace at once became an ordinary receptacle or container, being entirely free from any electrical function. I must say that this arrangement had been thought of by others for solving some other problems.

However, the system would have been unsuccessful if it had not been for the method of regulating the arcs. This was a little more troublesome, but I got over the difficulty by means of a third "electrode," consisting of a piece of wire in contact with the metal to be heated and connected to one terminal of each of two voltmeters, while the other terminals are connected to the poles of the dynamo.

I admit that "electrode" is a big name for that small piece



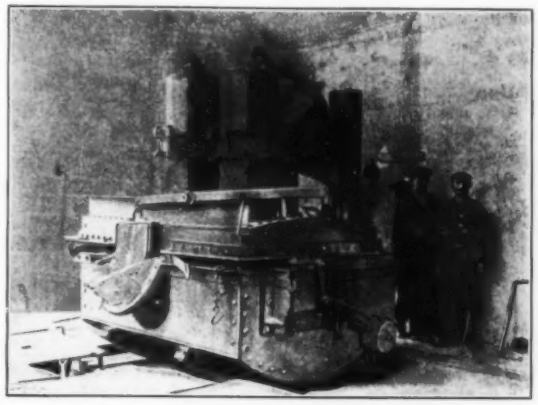
HEROULT FURNACE (U. S. PATENT 707,776).

From the carbon electrodes *d* the arcs jump to the metal. The bottom of the furnace is arched, and cogs on rails *g* engaging with cogs on rails *h* are arranged for effecting the tilting. For further details, see ELECTROCHEMICAL INDUSTRY, 1902, p. 63.

of wire, inasmuch as it is burnt away as soon as the furnace gets hot, but then it is replaced by the conductivity of the walls and bottom, which allow, owing to their great sectional area, a current of a few milliamperes to pass. In fact, all the regulation is automatic, and it is almost indispensable that it should be so, on account of the danger of spoiling the heat, by dissolving carbon from the electrodes.

This apparatus was extensively used for making low-carbon ferrochromium for some months. When it was first tried for iron, the efficiency was found very low; the apparatus had to be completed by a cover or lid so as to prevent the heat from radiating and being wasted.

As it stands in its present shape it looks very much like a Wellman furnace with two electrodes sticking in through holes in the cover. The furnace itself is built on two rockers,

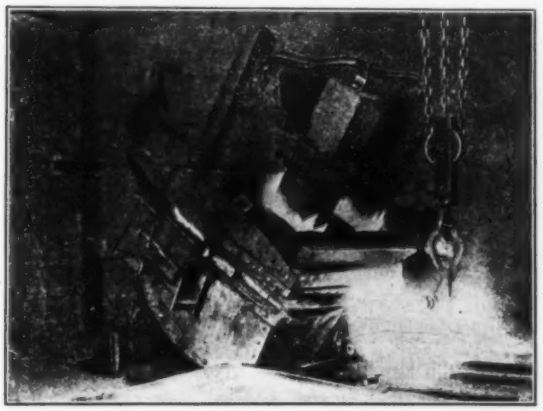


400 HP HEROULT FURNACE (LA PRAZ, 1903).

and by means of a hydraulic ram can be tilted so as to pour out its charge, "about three tons."

Having in my hands this instrument, I began, as might have been expected, to make bad use of it, viz.: trying the old problem of smelting steel or iron direct from the ore. This was, of course, a failure, the above-described furnace proving to be perfectly inadequate to that kind of work, chiefly on account of the corrosion of the walls and uncertainty of the final results of the operation. I decided, therefore, to divide the difficulty in two: first making cast-iron or pig, and afterwards treating said pig in the steel furnace. But now another difficulty arose, which was that we lost the principal advantage of the furnace by attempting to refine or oxidise part of the elements of the charge in an apparatus which was much more suited to melt down a charge in the absence of oxygen or oxidising agents.

The cast-iron problem was solved by means of another



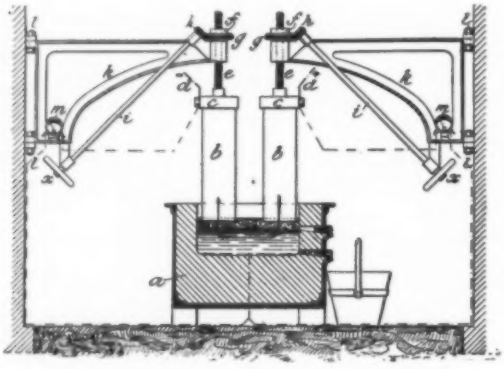
400 HP HEROULT FURNACE (LA PRAZ, 1903).

furnace, which did its work to the extent of 250 tons, which were sold. However, the process was laid aside for the time being, as more interesting for mine and hydraulic-power owners than for my company.

I then devoted my time and attention to the steel process, which proved to be of more immediate interest.

As it stands now it is chiefly used in the following way:

A charge of scrap iron, mixed or not mixed, with pig, is melted, either in the steel furnace itself or poured into it in the molten state from a ladle or from the fore hearth of a Wellman furnace or from a converter, the principal condition being that the molten metal should be suroxidised or overblown and free from slag. It is then covered with an artificial slag and submitted to the action of the current, which has no other object but to heat it up without any intervention of flame or oxidising agent of any kind. This enables me, by pouring out the first slag and charging new fluxes, to wash out all the impurities of the metal; by adding carbon and other ingredients a perfect deoxidation is obtained, and as a matter of fact the steel made by this process holds the record for purity. Perfectly deoxidised, traces of phosphorus and sulphur, all other elements at will, or to order, as one might



HEROULT FURNACE (U. S. PATENT 721,703).

The voltmeters *m* are in shunt with the two arcs between the electrodes *b* and the metal. For further details, see Electrochemical Industry, 1903, p. 287. Another furnace of Héroult is illustrated in the Analysis of Current Electrochemical Patents of this issue.

say, and all this made out of the most common kind of raw material; this is the result of the process in its present form.

I may add that outside of trials there have been made at this date about 1500 tons, of which 300 tons were produced in Sweden by the Aktiebolaget Héroults Elektriska Stal. This metal is tool steel, equal in quality to the best grade of crucible steel, and sold as such. The process is going to be applied to a large Thomas works, where electricity will be produced by a blast-furnace gas engine. The output of electrically treated metal is in France 6 to 7 tons a day, working on cold scrap; in Sweden, about the same, and with the Thomas combination it will reach 150 tons every twenty-four hours with one furnace, 5 ton heats, using 600 h.p. The consumption of electrodes is insignificant.

EXPERIMENTAL DETERMINATION OF THE SINGLE POTENTIALS OF THE ALKALI METALS, SODIUM AND POTASSIUM.

By Harrison Eastman Patten and William Roy Mott.

Nearly a century ago Davy discovered the alkali and alkaline earth metals. He isolated them by electrolysis of their fused salts. As another phase of the same subject, he determined an electrochemical series,[1] using dilute acids, as follows: + Potassium, barium, zinc amalgam, zinc ammonium-amalgam, cadmium, tin, iron, bismuth, antimony, lead, copper, silver, palladium, tellurium, gold, platinum, iridium and rhodium.

The potentials of alkali and alkaline earth metals have been obtained by amalgamating and determining the difference of potential between the amalgam and the solution used. The conception of a battery in which the anode is an alkali metal is not new. Goodman,[2] in 1847, used potassium amalgam as the plus electrode of a primary cell, which gave a total pressure of 3.23 volts.

Much excellent work has been done recently[3] upon the electromotive force developed by amalgams, of various concentrations, various metals and against different electrolytes. Still later, M. Sack[4] has determined the electromotive force of various amalgams, sodium alloys[5] and of sodium and sodium amalgam against lithium chloride dissolved in methyl alcohol at — 80°C. His references to the literature of the subject are very complete.

We have determined the single potentials of potassium and sodium against various electrolytes, both aqueous and non-aqueous. The electromotive force was measured by the Poggendorf compensation method, using as a zero instrument a Queen galvanometer, for which three-fourths scale division equals one-millionth of an ampere. A normal electrode whose voltage was taken as — .56 served as a half cell, to which connection was made through a strip of filter paper which had been saturated with the solution to be used. An asbestos shield afforded protection from fire, and the explosions which necessarily accompany the contact of potassium and sodium with water. The ignition of the hydrogen evolved by the metal was delayed by allowing only a small surface of metal to come in contact with the electrolyte. This afforded sufficient time to take several readings of the electromotive force. The single potential of metallic sodium and potassium, as experimentally determined by us, are given in the following table, together with some calculations of the theoretical single potentials.

Table I.—*Experimental Single Potentials.*

Electrolytes.	Potassium.	Sodium
KI in Acetone (Sat.)	2.35 V. 2.39	2.14 V. 2.14
NaI in Acetone (Sat.)	2.26 2.555 2.31 2.31	2.18 2.16 2.22 2.14
LiCl in Acetone (Sat.)	2.35 2.31	2.14 2.14
LiCl in Propyl Alcohol (Sat.)	2.23	2.05
LiCl in Ethyl Alcohol (Sat.)	2.29 2.29	2.16 2.155
LiCl in Pyridine (Sat.)	2.20 2.18 2.12 2.10	2.06 1.94 1.91 2.06
n KCl in Water	2.35 2.33 2.31 2.31	2.20 2.18 2.14 2.20
n NaCl in Water	2.32 2.29	2.14 2.13
39 % LiCl in Water (Nearly Sat.)	2.30 2.29	2.18 2.12

Theoretical Single Potentials.

Chlorides	2.38 V.	2.18
Sulphates	2.39	2.19
Nitrates	2.36	2.15

The above theoretical single potentials were calculated as follows: First, a calculation of the voltage of decomposition was made (from the heat of formation in dilute aqueous solution) for a chloride of some metal, such as zinc chloride, in the following table. From this value (2.44 volts) subtract the single potential of zinc[6] (as given by Neumann[6] for zinc in zinc chloride), + 0.503 volts and there remains — 1.94 volts as the single potential of chlorine.

[1] G. Gore, *Electrolytic Separation of the Metals*, p. 56.
[2] Alfred Daniell, *Physics*, p. 633 (1843).
[3] V. Türin, *Zeit. Phys. Chem.* 5, 340 (1890).
G. Meyer, *Zeit. Phys. Chem.* 7, 221 (1891).
H. P. Cady, *Jour. Phys. Chem.* 2, 551 (1898).
[4] *Zeit Anorg. Chem.* (1903) 34, 226, 252.
[5] F. Haber, *Trans. Am. Elect. Chem. Soc.* (1902) Vol. II., p. 189.
[6] *Zeit. Phys. Chem* XIV., 229 (1894).

TABLE II.

I.	II.	III.	IV.
$ZnCl_2$	2.44	+ 0.503	— 1.94
$FeCl_2$	2.16	+ 0.067	— 1.97
$CoCl_2$	2.05	— 0.015	— 2.065
$NiCl_2$	2.03	— 0.020	— 2.05

Similar calculations gave the above values for the single potential of chlorine, which may be taken as — 2.00 volts and which agrees well with the experimental determinations. And in like manner the single potential of the radical SO_4 is found to be — 1.85 volts, and that of NO_3 to be — 1.80 volts.

Second, the decomposition voltages of chlorides, sulphates and nitrates of potassium and of sodium were calculated from their heats of formation in dilute aqueous solution. These values are given below.

TABLE III.—*Theoretical Single Potentials of Potassium and Sodium.*

	POTASSIUM.			SODIUM.			
	D. P.	Pot. Rad.	Pot. K.	D. P.	Pot. R.d.	Pot. Na.	Pot. K—Na.
Chloride	4.38	— 2.00	+ 2.38	4.18	— 2.00	+ 2.18	0.20
Sulphate	4.24	— 1.85	+ 2.39	4.04	— 1.85	+ 2.19	0.20
Nitrate	4.6	— 1.80	+ 2.86	3.95	— 1.80	+ 2.15	0.21

In the above table, D. P. is the voltage of decomposition calculated from the heat of formation, as stated previously. Pot. Rad. is the single potential of the radical, as calculated in the previous paragraph. Pot. K, Pot. Na are the single potentials of potassium and of sodium, respectively. And Pot. K — Na is the difference in volts between the single potentials of potassium and sodium.

The following considerations indicate the reliability of our experimental determinations. Each of the values given for the single potential in Table I was obtained independently. Determinations were (1) repeated on the same specimen of metal, (2) on different specimens, (3) on fresh portions of the solutions and (4) on different days. (5) The single potential of zinc against normal potassium chloride was used as a check against our normal electrode. (6) Two observers did the work. (7) An examination of Table I. shows that the single potential of potassium is higher than that of sodium, and that, in general, the magnitude of this difference is of the same order as the difference observed between their theoretical single potentials in Table III. (8) Calculations based on thermal data confirm the experimental values. (9) The relative rate of action of the various solutions upon potassium and sodium varies greatly, and yet the single potentials are comparable throughout the whole series given in Table I. (10) A check as to the probable magnitude of the contact potential difference between the organic solution and the aqueous solution can be obtained from the work of Kahlenberg.[7] Consult further H. R. Carveth, on "Single Differences of Potential."[8]

From the preceding considerations, and from Table I. it is seen that the harmony observed between the theoretical single potentials and the experimentally determined values is greater than is to be expected from the statement on page 226 in *Le Blanc*.[9] "The value of magnesium, aluminium, and manganese, the water-decomposing metals, are only to be considered as lower limits, their action upon the water causing them to diminish immediately after introduction of the electrode." Magnesium and aluminium both have, as a rule, experimental values of the single potential some three-fourths of a volt lower than the theoretical values. Burgess and Hambuechen[10] explain this discrepancy as being due to the formation of a film upon the surface of the metal. Other analogous cases are those of chromium and zinc.[11] This explanation appears to us to be the true one. In electrolyzing lithium[12] out of pyridine, under certain conditions, we obtained a film similar to those present in the above cases. Sodium can be easily melted under pyridine, but soon coats over with a film. This suggests a reason why the lowest values in Table I are those for pyridine solutions.

Thus, the results in this paper strengthen the view that metals which give potentials lower than the theoretical do so rather because of the formation of a film upon them than because the metal decomposes the solution with liberation of hydrogen. The oxides and hydroxides of the alkalies, as well as their alcoholates, are soluble, so that we get no film, and the single potential observed is in fairly close agreement with the theoretical. At the same time, the hydrogen undoubtedly exerts some influence, but that this is small can be seen from the values of the single potential actually obtained.

In our work on lithium[13] we have found a fairly uniform decomposition voltage of four volts in various solvents. Subtracting from this the single potential of chlorine gives the single potential of lithium as + 2.0. But this is probably too low.

This work was done jointly in the Laboratories of Physical Chemistry and of Applied Electrochemistry, University of Wisconsin, Madison, Wis.

[7] Kahlenberg, *Jour. Phys. Chem.*, p. 379 (1899). Also, *Trans. Amer. Electrochem. Society*, 1902, Vol. II.
[8] *Jour. Phys. Chem.*
[9] *Electrochemistry.*
[10] ELECTROCHEMICAL INDUSTRY, January, 1903.
[11] Low values for zinc are given in the paper, Single Potentials of Zinc in Aqueous Solutions. *Trans. Am. Elect. Chem. Soc.*, Vol. III., 1903.
[12] Patten and Mott, The Role of Water in the Electrodeposition of Lithium from Pyridine and from Acetone. A paper read before the June meeting of the American Chemical Society, 1903.
[13] The Role of Water in the Electrodeposition of Lithium. The Deposition of Lithium from Various Alcohols. A paper read before the June meeting of the American Chemical Society.

PRODUCTION OF FLUORSPAR IN 1902.

From a report of Dr. J. H. Pratt to the United States Geological Survey, we gather the following information: There was a very large increase in the production of fluorspar in 1902 over that of 1901, which was partly due to its increased use for metallurgical purposes. The production in 1902 was 48,018 short tons, valued at $271,814, as compared with 19,586 tons, valued at $113,803, in 1901. Of this production 43,310 short tons, valued at $224,814, are reported to have been sold in the crude states, as compared with 15,450 short tons, valued at $77,500, in 1901, an increase of 27,860 tons in quantity and of $147,314 in value. There was an increase in price of both the crude and the ground fluorspar, the average price for the crude being $5.19 per ton, an increase of 19 cents over the 1901 price, and for the ground the price averaged $9.98, an increase of 76 cents over the 1901 price.

Besides the above production, there were 3520 tons of fluorspar mined, but not put on the market.

Cryolite, used in the manufacture of aluminium and sodium salts, is imported from Greenland. The imports for 1902 amounted to 6188 long tons, valued at $85,650, as compared with 5383 tons, valued at $70,886 in 1901, and with 5437 tons in 1900.

PIONEERS OF ELECTROCHEMISTRY—VI.

CHARLES S. BRADLEY.

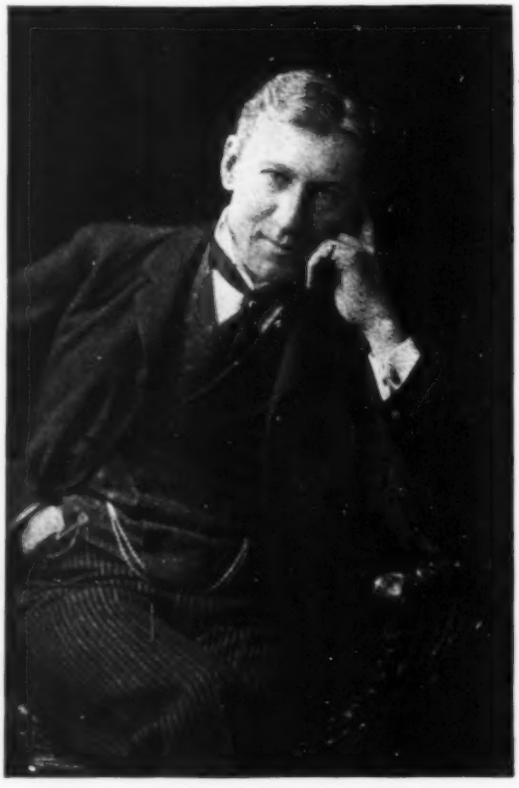
Mr. Charles S. Bradley will forever be cited among those few daring, impetuous pioneers in electrical engineering, who by putting into practice what they saw in visions and dreams have produced the phenomenal developments of recent years. Mr. Bradley is a broad man. While his name is justly mentioned among the pioneers of electrochemistry, the marks of his genius are found on all fields of electrical engineering. As Dr. M. I. Pupin, in a biographical sketch, once put it, Mr. Bradley was always connected with big things in electrical engineering, with huge experiments which proved huge successes.

Mr. Bradley was the engineer of the New York Edison Illuminating Company in 1881, and the success of this pioneer electric lighting company was due in a great measure to his inventive resources.

But the field of this company was too small for two such men, like Edison and Bradley, and the latter left the company to establish a small laboratory of his own in a little alley in Yonkers. This modest workshop became the birthplace of some of the foremost electrical inventions.

Here Mr. Bradley devised the method of multipolar windings, now so generally used for direct-current machines. The first multipolar machine in this country was constructed by him in 1887. When the engineers of the Edison works in Schenectady tested it, it created a profound sensation. The first synchronous converter was built by Bradley in 1888.

We mention these inventions merely to indicate the broad scope of Mr. Bradley's genius; he is one of the very few men who are masters in many fields. What Mr. Bradley has done for electrochemistry will appear in the following analysis of his electrochemical patents.



Charles S. Bradley.

One of the first patents granted to Mr. Bradley (312,802, Feb. 24, 1885) was for a storage battery with zinc-bromide as electrolyte and zinc and carbon as electrodes. The carbon electrode, at which bromine is produced during charging, is at the bottom of the cell; the zinc electrode is at the top.

This cell has later independently been re-invented by Mr. H. H. Dow, who described it in a paper at the inaugural Philadelphia meeting of the American Electrochemical Society. The only difference between Bradley and Dow is that the former uses a porous diaphragm, while the latter finds this to be unnecessary. In the discussion of Mr. Dow's paper it was remarked that the cell is old, but its original invention was erroneously attributed to Prof. F. B. Crocker.

As this mistake has gone into the printed Transactions of the society, it may be corrected here. Mr. Bradley was the first inventor of this battery, while Dr. Crocker was then his patent attorney. It is impossible that this cell may still have a future, especially for the purpose for which Mr. Dow wanted to use it, namely, as a standard cell. It can be set up most easily, anywhere on very short notice.

The mechanical construction of the cell was later modified by Mr. Bradley. His patent (409,448, Feb. 24, 1885) is interesting on account of the remarkable clearness with which the theory of metallic diaphragms is correctly given in very few words—a subject which was only recently again under discussion.

While these two patents prove Mr. Bradley's early and thorough understanding of electrochemical problems, the class of his "internal heating" patents is of enormously greater industrial importance. Without entering into the legal questions, we may simply mention that his internal heating inventions have been and are the subject of extended legal battles, first between Mr. Bradley and the Cowles Co., and now between the Cowles Co. and the Pittsburg Reduction Co.

The application for three patents (464,933, granted Dec. 8, 1891; 468,148, Feb. 2, 1892; 473,866, April 26, 1892,) was filed on Feb. 23, 1883; relating to the use of the electric current for producing a combined heating and electrolytic effect, and to the application of this method to the production of aluminium.

For the use of electric current to produce a pure heating effect in order to avoid external heating of crucibles, a patent was granted to Messrs. S. S. Bradley and F. B. Crocker on Feb. 2, 1886, the application having been filed on March 14, 1885. In this case alternating currents are, of course, available, and may be even preferable.

An electric furnace in form of a revolving wheel, now well known in the calcium carbide industry, was patented by Mr. Bradley on Jan. 25, 1898 (No. 597,945). The very important effect of this arrangement is to make the process continuous. An improved form of this rotary, continuously working type of furnace, was recently patented by Mr. Bradley (patent 723,643, March 24, 1903).

In recent years Mr. Bradley's inventive activity has been closely connected with the work of the Ampere Electrochemical Co. at Niagara Falls, and its offshoot, the Atmospheric Products Co. Mr. Bradley is now president of the latter company.

The enormous amount of experimental work done by the Ampere Electrochemical Co. and the success of which has largely been due to the inspiration of Mr. Bradley is well known to our readers. Among the processes worked out by this company are a process of Bradley and Jacobs for fusing bauxite in an electric furnace and thereby producing a pure artificial corundum, as now operated by the Norton Emery Wheel Co.; a process of Bradley and Jacobs for working barium sulphate into barium hydroxide, as well as processes for making artificial camphor, cyanides, silicides, etc.

What may be considered, however, as the crowning success of Mr. Bradley's recent inventive activity is his and Lovejoy's process for the fixation of atmospheric nitrogen from the air. This process has been described repeatedly in detail in this journal, so that this scant reference must suffice here. The process is certainly one of the most splendid achievements in electrochemistry, and may be hoped to have far-reaching and radical industrial and agricultural results.

From this brief sketch of Mr. Bradley's activity it appears that his inventive genius is nearly unlimited. The inventor of multipolar winding and of the synchronous converter is at the same time a leading electrochemist, and in the field of electrochemistry he is an equally daring and successful pioneer along many lines. May Mr. Bradley, who is still in the best years of his life, continue his splendid activity for many years to come.

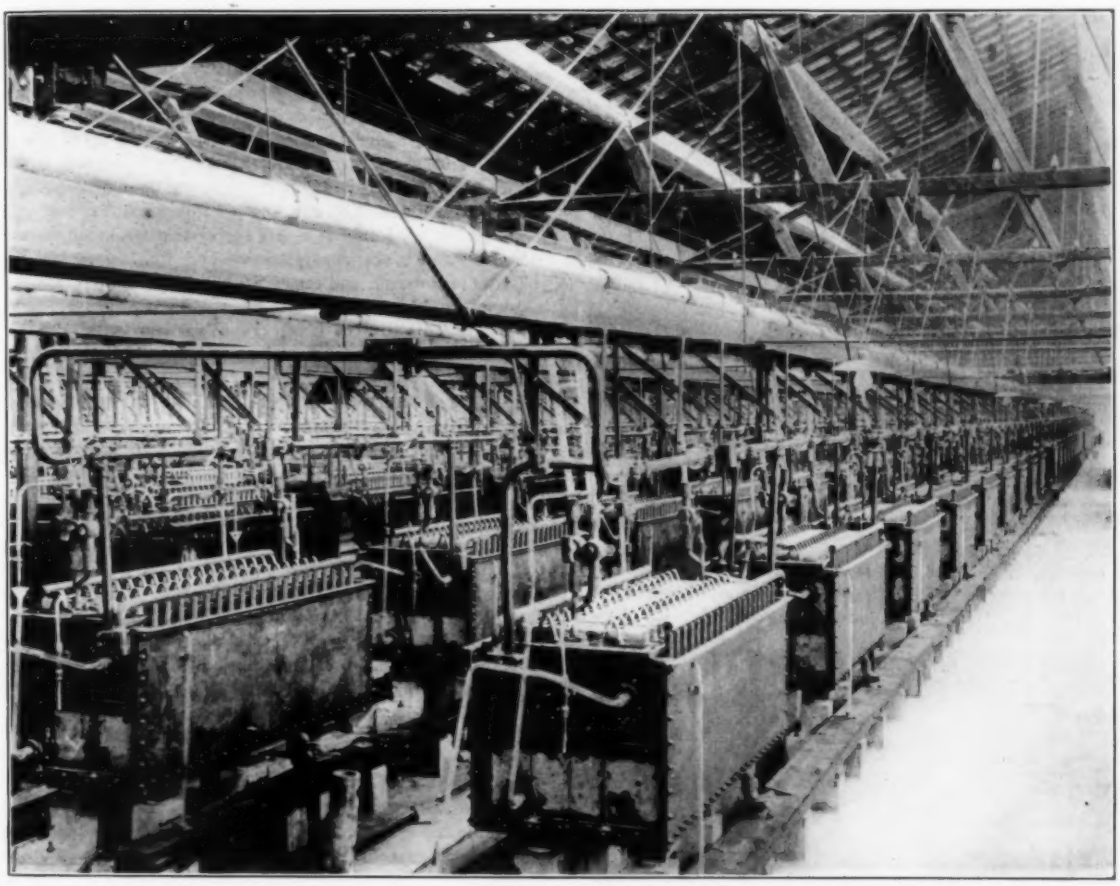
PLANT FOR MAKING BLEACHING POWDER AND CAUSTIC SODA BY THE DIAPHRAGM PROCESS.

The technical problems involved in the production of caustic soda and chlorine by electrolysis of sodium chloride have been solved by a great many inventors in quite different ways. The only commercially successful process in which *fused* salt is electrolysed is the Acker process. In all other processes in actual operation *aqueous solutions* are electrolysed.

The principal problem is always to keep the anodic and cathodic products of electrolysis separate from each other, and this problem has been solved in three essentially different ways. The first is to separate both compartments mechanically by a diaphragm (diaphragm processes); the second is to keep the anodic and cathodic liquids separate from each other by making use of their different specific gravities (gravity process); the third is to eliminate the sodium ions discharged at the cathode from the cell by alloying them with the cathode (mercury cathode process).

The mercury cathode process has been made a commercial success by Castner and Kellner; it is in use at the works of the Castner Electrolytic Alkali Co. at Niagara Falls. The gravity process ("Glocken process") is the latest of the three general classes of processes, and has found practical application only in Germany and Austria to a comparatively restricted extent. Diaphragm processes have probably found the most extended use. Mr. E. A. Le Sueur performed early pioneer work for this process in this country, while abroad the diaphragm process was developed mainly by the Griesheim company in Germany. At present the Dow Chemical Co., at Midland, Mich., is the largest manufacturer in this country using the diaphragm process, while other diaphragm processes are in use in various pulp and paper mills in the United States, notably in the New England States.

A characteristic feature of the whole class of diaphragm processes is the great variety of the details of arrangements of the electrolytic cells used by different inventors. This is due to the fact that the introduction of a diaphragm does not solve the whole problem, because after electrolysis has gone on for a while, caustic soda has been formed in the cathode compartment and begins to participate in the conduction of the current so that hydroxyle anions travel over to the anode compartment and produce reactions which are not wanted.



ELECTROLYTIC CELL ROOM FOR THE PRODUCTION OF CAUSTIC SODA AND CHLORINE, SOCIETA ITALIANA DI ELETTROCHIMICA.

This new problem is overcome by different inventors in different ways. We may note here, however, that this difficulty was clearly understood by Le Sueur in his early experiments; he counteracted this tendency of the OH ions by supplying fresh brine to the anode compartment and allowing bodily percolation through the diaphragm to occur under pressure.

In the following we give a description of an Italian plant in which a diaphragm process is used. As they are working under the Outhenin Chalandre patents, a brief description of this process, from United States patents 511,682, 647,217 and 665,953 may be here of interest.

As anode compartment a rectangular box is used; it is built of non-conducting plates, with rubber packing. A number of inclined porous tubes are arranged in vertical rows, and the vertical carbon anodes are placed between these rows of tubes. The cathodes are made in form of vertical sheet-iron combs, and the teeth of these combs extend into the porous tubes. A hood is provided for collecting hydrogen, cover-

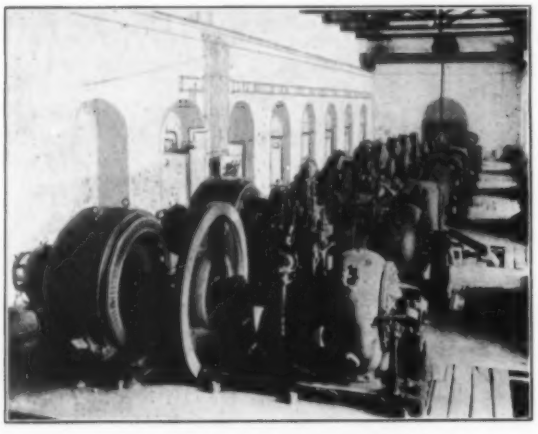
ing the higher ends of these tubes. Brine circulates between the anode compartment and a separate saturating vessel.

To counteract the tendency of the OH ions to do mischief in the anode compartment, Chalandre, Colas and Gerard utilize some of the hydrogen and chlorine which is developed in their electrolytic vats, to pass them into an outer chamber, where they are made to combine to form hydrochloric acid. This hydrochloric acid is supplied to the anode compartment to neutralize any caustic or decompose hypochlorite. The amount of hydrochloric acid used for this purpose is preferably 5 to 40 per cent of the amount of caustic produced in the same time.

PLANT OF THE SOCIETA ITALIANA DI ELETTROCHIMICA.

For the following information concerning the plant of the *Societa Italiana di Elettrochimica* and for the accompanying illustrations we are indebted to Sig. Cav. *Mario Michela*, in Rome. Fig. 1 gives an outside view of the plant, Fig. 2 shows the power plant, and Fig. 3 the electrolytic cell room.

The Societa Italiana di Elettrochimica has developed 6000



INTERIOR OF POWER HOUSE.

electrical hp. on the railway lines between Rome and the Adriatic Sea, and also has perpetual rights for 32,000 hp. more in the same place. The head of the waterfall is about 200 feet.

As mentioned before, the company works under the Outhenin Chalandre patents, using a diaphragm, which, after having been considerably simplified from its original construction, now is thoroughly satisfactory. They produce caustic soda of a high grade, viz., 75/77, and bleaching powder which is selling fairly well. However, the state of the market for the latter product is so unsettled that the company has decided to add a few more strings to their bow. They are now erecting supplementary plant for chlorates, pure synthetic hydrochloric acid, carbon tetrachloride, etc., from which they expect a better remuneration.

The Societa Italiana di Elettrochimica also has plants for sulphuric anhydride, under a license from the Badische Anilin und Soda Fabrik, and for other chemical products, which, however, are for the present out of the electrochemical field, but will, as they believe, be connected with it in the near future, after the development of more water-power.

MEASURING ELECTRODE POTENTIAL

By Woolsey McA. Johnson.

In a preceding article (Electrochemical Industry, July, 1903, p. 373) I tried to give some conception of the electrochemical quantity "electrode potential," and tried to show that it was as definite a physical quantity as the pressure of steam in a boiler, or the pressure of water against the walls of a dam. The reason that one conception appears usually hazy and indefinite and the other clear-cut and well defined is that "pounds per square inch" is a perfectly familiar expression known in childhood, while "e. m. f. against the hydrogen electrode" is used only in a few recent text books on physical chemistry and is not usually known.

If the phenomena and terms were equally familiar, the conceptions would be equally easy for the mind to grasp. In my articles on this subject I will try to explain facts by known facts and the theory will be found to be useful, but not indispensable.

The gist of the article in the July number was as follows:

(1) Whenever an electrode dips into an electrolyte, there we find a seat of e. m. f. acting either with the current or against the current, according to the direction of the current in the circuit.

(2) Conversely, whenever a current passes from the anode to the anolyte, or from the catholyte to the cathode, then chemical change ensues and the energy necessary to affect this chemical change is equal to the "electrode potential" of the system, when one coulomb had passed through the system.

The present article will describe the various practical and laboratory methods for measuring this quantity, both when made artificially or electrolytically. When made artificially, we have simply to measure the e. m. f. of a "galvanic cell." When made electrolytically we measure the "decomposition voltage" (Zersetzungspunkt) or the "polarization voltage" of the electrolytic cell.

The old-fashioned practical way of measuring the e. m. f. of a galvanic cell is to put a voltmeter across the terminals. The old-fashioned practical way of measuring the decomposition voltage of an electrolytic cell was similar, to put a voltmeter across the circuit, read the volts, open the switch and read the volts on open circuit.

Both these methods are excellent, if one condition is fulfilled. This one condition is that the measuring instrument takes such a small amount of energy that the potential of the circuit is not diminished. For instance, if we started to measure the e. m. f. of a two-ampere-hour lead accumulator, with a six ohm voltmeter we would get a rapidly diminishing reading, while if we used a high-resistance Weston voltmeter we would get a very accurate constant reading. If we had a cylinder of ten gallons capacity, charged with compressed air at 100 pounds and attempted to measure this with a leaky pressure gauge, we would find that the leakage through the gauge would diminish the pressure, so that no accurate reading could be taken. If, however, the gauge was tight and well-made, and if the pressure diminished, we might reasonably infer that the cause was some outside leakage, not through the gauge.

In any case the reading is only an approximation to the truth, because all instruments measuring the potential of a system absorb a fraction of the total energy, and that fraction diminishes to some extent the potential of the system.

The voltmeter method is only a rough approximation, but it is valuable, because it is easy to carry out, and especially valuable if we know that it is an approximation.

The best conditions for the method are as follows: First, the system should be as reversible as possible; second, the voltmeter should have a very high resistance. Both of these are but special cases of the condition cited above.

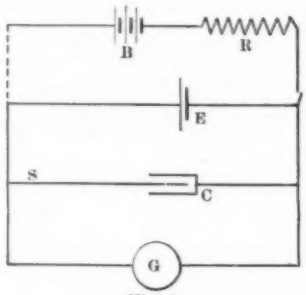


Fig. 1

CONDENSER METHOD.

If the system is very irreversible, or, to use the older term, polarizes quickly, we must use some instrument that absorbs only a modicum of energy. This is best done by availing ourselves of the static effects of electricity. An electro-static voltmeter, or the simpler form, the electrometer, can be used Perhaps, however, the best method is the so-called "condenser method" for measuring the e. m. f. of cells.

In Fig. 1 E is the cell whose e. m. f. we wish to measure. C is a condenser of about 1 or 2 microfarads capacity, S a two-way switch, and G a galvometer whose moving parts possess such inertia that the inertia takes all the "kick" on discharging C, and gives a reading functionally proportional to the quantity of electricity stored in C. Such a galvometer is called "a ballistic galvometer." For details of this instrument and method, the reader is referred to Carhart and Patterson's "Electrical Measurements."

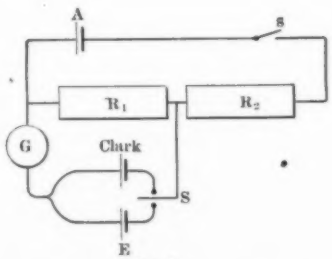


Fig. 2

POTENTIOMETER METHOD.

The method briefly described is first to charge C to a known potential, using a Clark or a Weston cell. By afterward discharging the condenser charged to this potential through G, the constant of the galvometer is found. The same procedure is followed substituting the unknown e. m. f. for the standard cell.

If the unknown e. m. f. is 1 volt, and the capacity of the condenser 1 microfarad, only 0.000001 coulomb of electric "juice" has been absorbed from the system. Such a small quantity can diminish its potential but slightly.

But, unfortunately, the electrode potential can drop of its own accord, just as the pressure of the air in the cylinder referred to above can decrease, not only through a leaky gauge, but through leaks in the cylinder itself.

To render this measurement more reliable, we must use some device that will charge the condenser at a definite period after breaking the main circuit (shown in Fig. 1, by B, the polarizing battery, and R, a resistance in series with it). Such a device is the Helmholtz pendulum, worked out by von Helmholtz several decades ago, with simple mechanical features. The period between break and make can be changed by one-millionth of a second steps. Such a method, with this refinement, is particularly desirable in measuring the electrode potential of a system in unstable equilibrium like the persulfation at the end of the charge at the anode in a lead accumulator. By varying the interval of time we can plot the curve of "auto-depolarization." This method can be recommended as the most accurate and scientific for measuring a rapidly changing electrode potential.

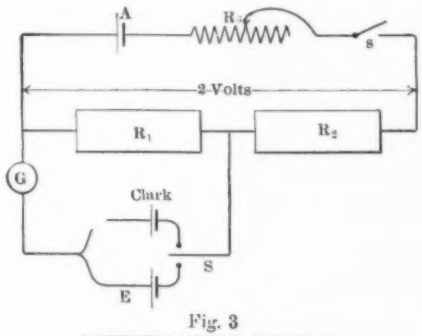


Fig. 3

POTENTIOMETER METHOD.

When the electrode potential does not vary by "auto-polarization" the "potentiometer" method is undoubtedly the most accurate method. In its simplest form, it is simply a known e. m. f. closed through a resistance box with a variable shunt circuit containing a galvanometer and the unknown e. m. f. connected so as to oppose the flow of current of the known e. m. f. By varying the resistances so that no current flows through the galvometer, we have the drop in voltage across that part of resistance in multiple with the shunt circuit exactly equal to the unknown e. m. f. It goes without saying that the known e. m. f. should be larger than the unknown e. m. f.

In a slightly more complicated form it is shown in Fig. 2. An accumulator A is placed in circuit with two 10,000 ohm resistance boxes R_1 and R_2. Around R_1 is a shunt circuit consisting of a sensitive galvonometer G and in series with either a Clark cell or the unknown e. m. f. E. The two-way switch S allows putting in the circuit at will, either the Clark or E.

The procedure is to close *s*, and throw in the Clark by S,

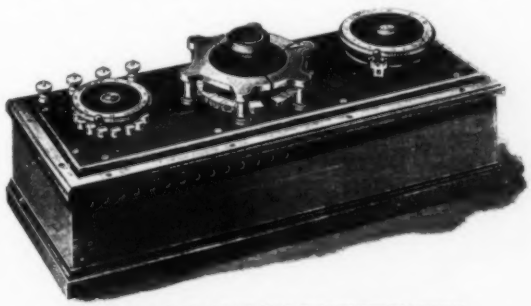


FIG. 4.—DIRECT-READING POTENTIOMETER.

then to vary R_1 and R_2, so that their sum is exactly 10,000 ohms, and that R_2 is of such a value that no current flows through G whose needle must then point to zero. Then, if the e. m. f. of the Clark standard cell be taken as 1.433 volts at 15° C., the e. m. f. of A is found thus:

$$\frac{\text{e. m. f. of A}}{\text{e. m. f. of Clark}} = \frac{R_1 + R_2}{R_1}$$

for as the system is in equilibrium the voltages are proportional to their resistances. Then we have voltage of $A = 1.433 \frac{10{,}000}{R_1}$, because $R_1 + R_2 = 10{,}000$ ohms, and the e. m. f. of the Clark cell = 1.433 volts.

If the temperature of the Clark cell be not 15° C., but t° C., the true e. m. f. can be found by the formula $E_t = 1.433 - 0.012\ (t-15)$ volts.

If, instead of the Clark cell, the Weston cell be taken, its e. m. f. is $E_t = 1.0186 - 0.00004\ (t-20)$ volts.

The temperature-coefficient of the e. m. f. of the Weston cadmium cell is so small that a change of 25° C. makes only a difference of a millivolt. Accordingly for all ordinary work, the e. m. f. of the Weston cell can be taken as 1.019 volts at room temperature.

Having found the e. m. f. of A, the secondary or working standard, S is now thrown so as to put E in the circuit. If the e. m. f. of E is known roughly, it is easy to make R_1 about the right value. This will naturally save considerable manipulation of the plugs. One set of plugs should be removed and put away. Then, whenever one plug is removed from one resistance box it should be placed in the corresponding hole in the other. Thus the sum of R_1 and R_2 is kept at 10,000 ohms without much mental labor. Now we have, if we make the new value R_1^1 so that the galvanometer needle is again at zero, $\frac{\text{voltage of E}}{\text{voltage of A}} = \frac{R_1^1}{10{,}000}$, hence the e. m. f. E in volts is $E = \frac{1.433}{R_1} R_1^1$.

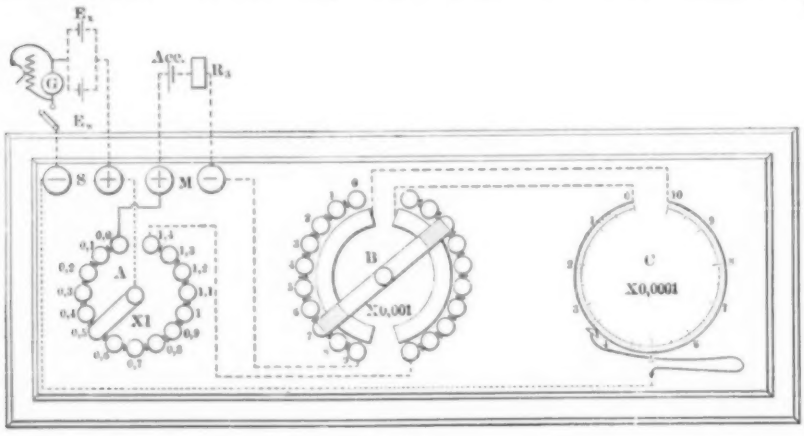


Fig. 5

CONNECTIONS IN DIRECT-READING POTENTIOMETER.

From this relation it is seen that if R_1 were divisible by 1.433 an even number of times, as 1000, we should get the value of E from the resistance R_1^1 by the simple operation of pointing off.

It is quite easy to make R_1 divisible by 1.433 an even number of times by putting in series with A a resistance. If this resistance is so chosen that the drop through R_1 and R_2 is 2 volts, then 5 ohms in R_1 will correspond to one millivolt. A simple arithmetical calculation will show this to be the case, if in the comparison of A with the Clark cell the value R_1 were made 7.165 ohms, and the third resistance R_3, seen in Fig. 3, adjusted so that G showed no deflection.

Such an apparatus can be set up out of ordinary resistance boxes, and will do excellent work. But by far the best is to have them combined in one instrument so that all the parts fit each other. I have considerable experience with several of these so-called "direct-reading potentiometers." The simplest and cheapest was made for me by Dr. R. Franke, of Hanover, Germany, and is shown in Fig. 4.

Its greatest drawback is the fact that its total resistance is only some 1500 ohms. Now, most accumulators will polarize to some extent in the millivolts in five minutes, if closed through 1500 ohms. This objection to the method I overcame by making a Plante cell of large electrode surface with a large amount of electrolyte, and with the lead only formed very slightly. Now, if the electrolyte in pores of the electrode becomes dilute by sulfation of electrolytic action, it will be easily replaced by the large amount of acid that will diffuse readily through the *thin* layer of active material. As the e. m. f. of a lead accumulator depends on the strength of acid in the active material, if that acid be kept constant, the e. m. f. will be constant.

Fig. 5 shows the scheme of connections in the Franke direct-reading potentiometer.

The first resistance A consists of 1400 ohms with taps coming at intervals of 100 ohms to a circular series of German silver contact knobs. A contact brush revolving over the tops of these knobs allows any step from 0 to 1400 ohms in 100 ohm intervals.

B is a second resistance of 180 ohms, arranged similarly in 10-ohm steps, but with a double-contact brush, so that only 90 ohms is in the main circuit, and any resistance in the series 0, 10, 20, 90 ohms in the shunt circuit. C is a circular revolving resistance of even calibre with a slide contact. The resistance C is always in the main circuit, which thus is ever equal to 1500 ohms. The part of C in shunt circuit is read on the scale of this circular bridge wire. The mechanical arrangement can best be seen by glancing at cut, Fig. 4.

Acc is the special lead accumulator, R_2 is the adjustable outside resistance of such a value that 1.500 volt is the drop through A B C. Thus the drop through one ohm is exactly one millivolt or 0.001 volt. Ew is the Weston standard cell, and Ex the cell whose e. m. f. we wish to measure.

The method is nearly the same as in the preceding method. As a Weston cell is used whose e. m. f. is 1.019 volts, we put

A at 1,000 ohms
B at 10 ohms
C at 9 ohms

total R_1 = 1,019 ohms, corresponding to 1.019 volts.

R_2 is then adjusted until G gives no deflection.

The galvanometer had best be connected with a small variable shunt resistance. At first the shunt resistance is made small so that only a small fraction of the current flows through the galvanometer. Thus only a fair deflection of G's needle is made. As the adjustment on the potentiometer becomes finer, this resistance is increased and finally, when the balance is nearly reached, the shunt can be cut out and the galvanometer is used in its most sensitive condition. If no shunt were used, the galvanometer might be seriously injured by using it with too high a voltage.

Another method might be used to change the sensitiveness of the galvanometer. I have never used this method in electrolytic work, but have found it very useful in other work. This is to have the field of a d'Arsonal galvanometer not set up by a permanent magnet, but by an electromagnet. By having a variable resistance in series with this electromagnet, the

strength of the field can be varied by varying this resistance.

Having adjusted the instrument so that exactly 1.500 volts is delivered at the terminals, Ex can be thrown in and measured by moving the revolving contacts until the galvanometer shows no deflection.

The only "contact resistances" that vary the *resistance of the main circuit* are the two of B. These contacts are accordingly made large, as can be seen in Fig. 4. The resistance of contact should never be higher than 0.01 ohm, which would mean 0.0001 volt—of course a quantity too infinitesimal to be measured. The other resistances are in outside shunt circuit, and even if they were large, could only have the effect of diminishing the sensitiveness of the galvanometer.

If we know the approximate value of Ex we can set A and B at right shunt values, and often do all the adjustment on C. In any case we can read the e. m. f. in volts directly from the positions of the revolving contacts of A, B and C. Hence the name direct-reading potentiometer.

The preceding methods enable one to measure the e. m. f. of an electrochemical system, or, in other words, to measure the difference of "electrode potential of two electrodes." Both these methods usually measure the e. m. f. of the cell when the cell is inactive, and no current is passing through it. The cell can be made either chemically or electrochemically. The following method measures the electrode potential of a cell as a result of electrolysis, by measuring the amperes as a function of the impressed volts. Simply a voltmeter is placed across the cell and an ammeter in series with cell. The method is to determine the "characteristic" curve of the cell.

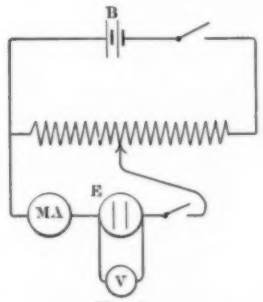


Fig. 6

MEASURING DECOMPOSITION VOLTAGE.

The usual term is measuring the "decomposition voltage" (Zersetzungsspannung). In Fig. 6 we see the diagrammatic sketch of the apparatus.

B is a battery of two lead accumulators, with a switch, and R is a resistance (with shunt) of about 200 ohms. (M A) is a milliammeter of low internal resistance. E is the cell whose decomposition voltage we wish to measure. (V) is a *high resistance* voltmeter reading to 3 volts. For both M A and V proper galvanometers can be substituted, but Weston instruments are by all odds the best. R can well be a cylindrical Kohlrausch bridge, and its reading will give that part of the 4 volts applied to the shunt circuit.

To take a concrete example we will now consider that we are measuring the decomposition-voltage of the halogen acids—HCl, HBr and HI. The cell can well be a small breaker of 200-cc capacity, through whose wooden cover are led two platinum wires sealed in glass. These wires should be about one-half an inch apart.

It must be remembered that we are creating two new electrodes and measuring the difference of electrode potential of these two new electrodes. In the case of HCl, hydrochloric acid, we measure the difference of potential between electrolytically formed hydrogen in platinum and electrolytically formed chlorine, also in platinum.

Should we wish to measure the potential of one new electrode, we can have recourse to two methods; we can either make the electrode whose potential we wish to measure very small in comparison to the other; this will remain constant and we measure the change in other; or we may put in cell a third auxiliary electrode and measure the voltage of each against this.

The test cell is now filled with normal hydrochloric acid. We next impress upon E a voltage of 0.05 volt, as seen on the bridge reading, wait ten seconds and read both V and MA. The impressed voltage is increased by steps of 0.05 volt, and in each case after 10 seconds the voltage and amperage are read. At first, there is seen a very small deflection of the ammeter, which does not increase until 1.30 volts have been reached. Here the pointer of the ammeter begins to show signs of life. We now increase the voltage by steps of 0.01 volt, and soon the ammeter begins to increase rapidly. When 1.45 volts are reached the test has been completed. On plotting the readings it will be found that the curve is in a boomerang shape. One limb of the boomerang is near the X-axis. At about 1.30 volts the curve seems to take a bend (more or less sharp), and the other limb of the boomerang is seen mounting nearly vertical. By drawing a tangent to both limbs it will be found that the tangents intersect each other at 1.31 volts. This value 1.31 volts is the so-called "decomposition voltage" of hydrochloric acid, and is a measure of the electrical energy necessary to break up hydrogen chloride. It is also a measure of the force with which the hydrogen ion and the chlorine ion are bound to each other by the means of the solvent water.

The dynamical relation between anion, cation and solvent is unknown, but in the nature of things it is some form of a closed polyhedron. When the strain on any member of the figure exceeds the force, binding the figure together, we have disruption. It is quite a pretty coincidence that the curve of "decomposition voltage" of hydrochloric acid resembles the curve made in finding the "elastic limit" of steel for example. In each case, when the force exerted on the system from the outside is large enough to overcome the cohesive force of members of the system, "something has to go" and it does go. In each case the point is not sharp and varies with the method.

We will now replace hydrochloric acid with hydrobromic acid, and the decomposition voltage is found at 0.94 volt. When hydroiodic acid is used the "voltage" is found to be 0.52 volt. In each case we can see the visible electrolysis at the same time the ammeter reading begins to increase. When 0.53 volt is rached with HI heavy brown clouds of iodine can be noticed descending from the anode.

Now, if we use HCl solutions of different concentrations the "decomposition voltage" will be found to vary. LeBlanc gives these values:

2n HCl	1.26 volts.
n HCl	1.31 volts.
½n HCl	1.34 volts.
1-6n HCl	1.41 volts.
1-16n HCl	1.62 volts.
1-32n HCl	1.69 volts.

With 1-32 HCl we have reached a point where no longer Cl is given off but a large proportion of oxygen.

Naturally in the electrolysis of brine, or of $ZnCl_2$ or $NiCl_2$, with the production of chlorine at the anode, the curve of electrolysis should be studied. The results should be expressed, not in "amperes per square foot," but in electrode potentials.

If the brine contained with NaCl a proportion of NaBr and NaI, it would be perfectly possible to partially separate these electrolytically from the NaCl and from each other, just as it is possible to partially separate copper from nickel electrolytically at the cathode or in the case of a soluble metallic anode, silver from copper, gold from silver or platinum from nickel by "sliming" the less electropositive metal.

In almost all cases the separation is not complete, but only a concentration product is formed.

So the concentration product containing Br and I could be subjected to a second electrolytic action and a higher concentration product obtained. Finally the treatment could be carried on chemically with cheap brine, and cheap power; there would be a wide margin of cost when the high-selling price of Br and I are considered.

The above is mentioned merely to show how important it is when attacking any practical proposition to know fundamental scientific facts. In a further article I will discuss the various standard electrodes, and treat of electrode potential from the standpoint of thermodynamics and the dissociation theory.

THE ST. LOUIS WORLD'S FAIR AND ELECTROCHEMISTRY.

Since the 1902 convention of the American Electrochemical Society at Niagara Falls, at which time a participation in the Universal Exposition in 1904 was first discussed in the Society, developments have been rapid and convincing on the World's Fair grounds in St. Louis.

To those who have not been fortunate enough to visit the exposition grounds within the last two months, the illustrated journals give at best but a poor idea of what the exposition is and is to be. To use the words of Commissioner General Lagrave, of the French Republic, to the Louisiana Purchase Exposition, "The site is ideal in the extreme." All of the sixteen great exposition buildings will be completed by the first of October, and seven of them are completely finished to-day.

It is well worth the while of any one who may find himself within easy reach of St. Louis to visit the grounds, and see for himself the great scale of progress made upon the exposition.

The Electrochemical Exhibits.

It is gratifying to know that the present space requirements of the electrochemical exhibits exceed 10 per cent of the exhibit area of the palace of electricity. The present prospects have far outrun the hopes which were entertained last year.

Among the exhibitors are the pioneers in electrochemistry, and some of the most vigorous representatives of the Niagara Falls electrochemical colony.

Whole processes will be shown, and the display in its entirety will be well worth the study and consideration of the electrochemist, and deserving of inspection, even to the limitation, should time demand, of the other elements of the exposition.

There will also be a number of important electrochemical exhibits shown in the building devoted to mines and metallurgy. Close co-operation between the chiefs of this department and the electrical department is insuring the success of the details of the various exhibit schemes which are being carried into effect. These departments are also organizing a plan for a demonstration, at the time of the International Electrical Congress, of special features, in a temporary building to be placed on the hill back of the Palace of Mines and Metallurgy, this site being available as well as readily accessible.

Exhibit of the American Electrochemical Society.

We wish to urge upon the membership of the Society the necessity of responding promptly to the request recently sent out by Secretary Reed on behalf of the Society's committee for an historical electrochemical exhibit. Such an exhibit will greatly redound to the credit and advantage of the Society, which ought to be represented in an appropriate and dignified way by an exhibit commemorative of the development of electrochemistry in conjunction with similar exhibits which are being prepared by presentation by the American Institute of Electrical Engineers, the British Institution of Electrical Engineers, besides four of our other national American engineering societies. President Richards is the chairman of the Society's committee having charge of the preparation of the exhibit, and all persons who can contribute or know of important electrochemical apparatus should communicate with him as soon as possible.

The International Electrical Congress and the American Electrochemical Society.

The International Electrical Congress has now reached such definite proportions that its success is entirely assured. The fact that it is organized with Prof. Elihu Thomson as president, Mr. B. J. Arnold as vice-president and chairman of the executive committee, and Dr. A. E. Kennelly, of Harvard, as secretary, assures that it will demand recognition abroad as well as at home.

The congress will consist of two important divisions: First, a chamber of official delegates made up of representatives of the great world powers, upon invitation of the United States Government, to take up for discussion all matters that are of international importance and affecting the electrical industry; second, the general electrical congress participated in by the members of the European and American electrical associations. The general congress will be divided into a number of sections, and these sections, through co-operation of our national electrical bodies, will be organized with the full support of the branches of the science which they cover.

The annual conventions of all of our prominent national electrical organizations will be held in St. Louis in conjunction with the congress, and will hold joint sessions with appropriate sections of the congress. This naturally will place the American Electrochemical Society in the position of being sponsor for the electrochemical section of the congress, and will present a most gratifying opportunity for bringing the Society into the closest and most harmonious touch with all the prominent electrochemical movements of the world.

The time seems ripe and the opportunity at hand for the bringing about of the concourse of electricians such as the world has not before seen. We congratulate the Committee of Organization of the International Electrical Congress of 1904 on the plan and scope of the scheme which it has developed, and we congratulate the Electrochemical Society upon having joined so heartily in supporting all the movements.

INTERNATIONAL CONGRESS FOR APPLIED CHEMISTRY.

Report of the Proceedings of Section X.

(Electrochemistry and Physical Chemistry.)

By H. Danneel, Ph. D., and J. K. Clement.

First Meeting (June 3).

The section was welcomed by the president, Dr. Boettinger, of Elberfeld. The first paper was presented by Traube entitled:

An Investigation of Critical Density.

The author formulated a theory that the gaseous and fluid molecules of a substance are quite distinct from one another, and that especially their individual volumes, which are represented in Van der Waals' formula by b, are very different. A fluid, according to this theory, is a solution of gas molecules or "gasons" in "fluidons," whereas a gas is a solution of the latter in the former. The solubility of the one in the other increases with rise of temperature, and the solubility curves meet at the critical point.

The experimental proofs which the author gave in support of his theory are chiefly as follows. Glass bulbs of different known density were enclosed in a tube filled with pure carbon tetrachloride, and this was heated in a thermostat to a point above the critical temperature. It was observed that at 10° above the critical temperature the bulbs remained still floating for hours at different heights. At a point several degrees above the critical temperature, differences in density of 50 per cent and more were shown.

In the discussion which followed, and in which Teichner, Kistiakowsky and Traube participated, Tammann pointed out

that the presence of small quantities of impurities would account for these phenomena.

THE DETERMINATION OF MOLECULAR WEIGHTS AT HIGH TEMPERATURES.

This paper, presented by W. NERNST, dealt essentially with the same subject as his paper presented at the New York meeting of the American Electrochemical Society (ELECTROCHEMICAL INDUSTRY, May, p. 319; Transactions of the American Electrochemical Society, vol. III., p. 75). Some additional results were, however, given which Nernst has obtained in the meantime. Sulphur, at the high temperature of the experiments, is appreciably dissociated, at least 45 per cent of S being dissociated at a temperature between 1900° and 2000°. It is possible that at high temperatures the three-molecule S_3 may be formed in a manner analogous to the formation of ozone (O_3). Sulphur dioxide was found to be stable up to 1950°. At such temperatures silver has vapor pressure considerably below atmospheric pressure.

A NEW ELECTRICALLY HEATED RESISTANCE FURNACE.

The furnace described by O. FROEHLICH is made of stoneware, the conductivity of which, at ordinary temperature, is sufficiently large to permit the flow of the current necessary to warm it. With rise of temperature the conductivity increases and the furnace is said to bear a temperature of 1600°. The material of the furnace has also the property of retaining the heat to a marked degree. No important particulars regarding the furnace were given as a patent has been applied for.

In the discussion Drossbach remarked it is wrong to believe that up to the present a material is not known which does not conduct when heated. Pure oxides are practically non-conductors, and conduct only when impurities are present. Nernst confirmed that under 1800° oxides are non-conductors; thorium and magnesium oxides only conduct when mixed. There are in fact only a few oxides that have not been experimented upon in this direction (see Reynolds, *Jahrbuch der Electrochemie*, vol. 7, p. 151, 1900).

SECOND MEETING (JUNE 4).

COLLOIDAL ZIRCONIUM.

A paper on this subject was presented by E. WEDEKIND. When zirconium earth (ZrO_2) is reduced by smelting with aluminium a product is obtained, which, on treatment with water, gives a blue fluid containing colloidal zirconium. The zirconium in solution is not precipitated by electrolytes, but by H_2O_2 (hydrogen peroxide), the latter not being destroyed by the colloid.

In the discussion Whitney remarked that colloidal zirconium has the property, which other metallic colloids are known to possess, in that under the influence of an electromotive force it migrates in the direction opposite to the current.

METALLIC CARBIDES.

In a paper on this subject H. MOISSAN, of Paris, whose work on inorganic syntheses in the electrical furnace is so well known, gave a resumé of his experiments with metallic carbides. The various particulars which he gave have already appeared in the *"Comptes Rendes de l'Academie des Sciences."* There was no discussion.

ELECTROLYTIC REDUCTION OF UNSATURATED COMPOUNDS.

A paper on this subject was presented by C. MARIE. The addition of hydrogen to unsaturated hydrocarbons can easily be performed by means of electrolysis when the proper cathode is chosen. With mercury as cathode it is possible to convert unsaturated acids, such as fumaric, cinnamic, aconitic into the corresponding saturated acids.

In order to avoid oxidation at the anode, the author makes use of the following apparatus. A layer of mercury is brought into a wide vessel, the bottom of which is formed by a diaphragm, and upon the mercury is brought the solution to be reduced. The vessel is placed in a solution of caustic soda, and is connected with a battery, the negative pole with the mercury, and the positive with an electrode immersed in the solution of alkali. Under these conditions amalgam is continuously formed which acts as the reducing agent.

In the discussion Elbs remarked concerning cinnamic acid that this acid is oxidized with difficulty into benzaldehyde and carbon dioxide, but is easily reduced to phenylacetic acid. The difference between both process is so great that if no diaphragm is used, very little benzaldehyde is formed, while the yield of phenylacetic acid is almost quantitative.

THE IMPORTANCE OF ELECTROLYSIS FOR THE PREPARATION OF INORGANIC COMPOUNDS.

A paper on this subject, presented by F. FOERSTER, was an account of the uses of electrolysis for the manufacture of inorganic substances, and of our present knowledge concerning the mechanism of electrochemical action at the electrodes. It is not possible to give an abstract of this condensed report without translating it almost word for word. Attention, however, might be called to the fact that ceric sulphate ($Ce(So_4)_2$), as an oxidizing agent, stands very near to permaganic acid relative to its oxidation potential. The ceric sulphate can be regenerated by means of electrolysis, from the cerous sulphate $Ce_2(SO_4)_2$ formed. This material appears to have a great future on account of its strong oxidation properties, and the ease with which it can be regenerated. Bright platinum foil in a solution which contains 0.1 grammolecule of Ce $(SO_4)_2$, and 0.05 grammolecule of $Ce_2(SO_4)_3$, and which is normal relative to H_2SO_4, has a potential of—1.45 volts against the hydrogen electrode.

In the discussion Loeb inquired how Foerster would explain the fact that copper anodes in a chloride solution give monovalent cuprous ions, whereas in a neutral solution of copper sulphate bivalent cupric ions are formed. Foerster in reply said he believed that at first always monovalent ions are formed, and that these are much more stable in the chloride solution than in nitrate, on account of the formation of complex ions in the former.

Wohlwill agreed with Foerster that at first the simplest ions are formed, but that they only remain when they are stable in the respective solutions. For example cuprous ions are unstable in nitrates and sulphates, and are immediately transformed into metallic copper and cupric ions. In other cases phenomena take place, which are not yet explained. For instance, we do not know why Sn in H_2SO_4 always goes into solution as bivalent ion. Whereas in other solutions the tetravalent ion is formed.

Pure gold is dissolved usually as univalent ion in chloride solutions, but if alloyed with platinum, it forms trivalent ions.

THE IMPORTANCE OF ELECTROLYSIS FOR THE PREPARATION OF INORGANIC COMPOUNDS.

This communication, by BRANDEIS, was a condensed account of the application of electrolysis to the manufacture of inorganic chemical compounds, and does not lend itself to a further abstract.

ELECTROLYSIS BY MEANS OF ALTERNATING CURRENTS.

A paper presented by LEBLANC gave an account of an investigation of the assumptions made in Richards' and Roepper's patent on this subject. It is maintained by the inventors that by electrolysis of a hyposulphite solution between cadmium electrodes by means of alternating currents, a good yield of cadmium sulphide is obtained. By the impact of the current in one direction on the electrode cadmium sulphide is said to be formed, while by the next impact of the current in the opposite direction hydrogen is formed which forces the CdS from the electrode and causes it to drop to the bottom.

LeBlanc and Schick found, however, that a current of 10.0 alternations per minute (i. e., a frequency of about 8 periods per second), and a current density of 4.6 amperes per square centimeter gave practically no yield. A smaller frequency gave

better results, and an efficiency of 75 per cent was obtained with one alternation per minute, the solution at the same time being well stirred.

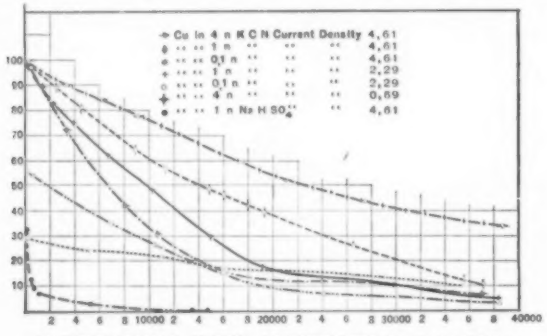
With direct current and abundant stirring a theoretical yield of CdS was obtained. From these results it appears that the CdS which had been formed anodically, undergoes cathodic reduction, and that the yield obtained with low frequencies is due to the fact that the sulphide is removed from the electrode by stirring and cannot be reduced.

Researches of this kind enable us to form some idea of the rate of reaction in inorganic solutions, a subject on which very little is known. If a copper electrode is electrolyzed in KCn solution two cases are possible. First, if the alternating current has a very low frequency, the copper, while anode, goes into solution by the impact of the current, and dissolves in the KCn. When the direction of the current is then reversed, copper is not deposited back, for out of a solution of KCn containing Cu the H is given before the Cu, this being due to the formation of a complex compound which makes the concentration of the copper ions very small. The second case is that the impacts of the current follow one another so quickly that the copper has no time to combine with the CN ions, and by the next impact of the current the copper is redeposited.

In the first case the copper electrode is dissolved according to Faraday's law, and in the second the copper electrode behaves like a platinum one and remains as it was.

If the number of alternations be varied and the two numbers found for which the copper is dissolved according to Faraday's law, and for which it remains unaltered, then the velocity of the reaction between Cu and CN must lie between the two half-periods which correspond to the numbers of alternations.

In each experiment the frequencey was varied between 1 and 4000 alternations per minute. The results of one series of experiments are given in the adjoining diagram, in which the



ELECTROLYSIS WITH ALTERNATING CURRENTS.

current efficiency is given in per cents as function of the number of alternations per minute. The diagram also shows the influence of a change of concentration, and of a change of current density.

The velocity with which the copper ions react is very great, but is nevertheless capable of comprehension. When copper ions in a solution of 0.1 normal concentration are brought together with a potassium cyanide solution of 4 to 1 normal concentration the reaction is nearly completed within a thousandth part of a minute. By means of exterpolation the author estimates that with 80,000 alternations per minutes, and a current density of 4.6 amperes per square decimeter in a 4 normal KCN solution, no copper remains in solution.

If copper ions in 1-800 normal concentration come together with 4 to 1 normal potassium cyanide solution the author estimates that after 1-80,000 part of a minute the reaction had hardly begun. From these two limit numbers we obtain an idea of the velocity with which the reaction takes place.

In the discussion which followed Krueger remarked that the polarization capacity of a mercury electrode, in KI or KCN solutions, along with the corresponding mercury salts, varies in a manner different from that which would follow from Warburg's theory in which diffusion is assumed to play the chief part. It is possible that the velocity of reaction is the controlling factor.

Wohlwill inquired if diffusion did not play an important part in LeBlanc's experiments. To this LeBlanc replied that experiments made with copper electrodes in solutions where no complex ions were formed show that for a frequency of from 1 to 2000 per minute practically no dissolving of copper is observed, and that the influence of diffusion has therefore already disappeared.

Nernst believes that by the method indicated by Krueger it is possible to arrive at a perfect theory. He pointed out that LeBlanc makes the silent supposition that the velocity of the dissociation of a water molecule into hydrogen and hydroxyl ions is infinitely great, compared with the velocity of dissociation of the complex ions into Cu and CN ions. LeBlanc agreed that this supposition is made, but gave the grounds upon which it is based.

Remarks on the Electrometallurgy of Aluminium.

G. Gin, of Paris, spoke of the physical and chemical conditions necessary for electrolytes used in the industrial preparation of aluminium. His communication, however, comes rather "post festum," for these conditions have for some time been well known. The electrolytes must possess a low melting point, must be very fluid when melted, must have a lower specific gravity than aluminium, and low-vapor tension and minimum electrolytic resistance. Chemically the electrolyte must belong to the least exothermic compounds. The energy required for the preparation of aluminium depends upon the resistance of the electrolyte, and upon the electromotive force of polarization. The calculation of the amount of this e. m. f. from the heat of reaction gave for Al_2F_6 2.49 volts, Al_2O_3 2.19 volts, Al_2S_3 1.27 volts. The calculation, however, is incorrect, because the e. m. f. should be found from the Gibbs-Helmholtz equation, and not from Thomson's rule. The author finds that the difference in the consumption of energy by the various proposed electrolytes hardly amounts to a cent per kilogram of aluminium. In consequence, the cost of making aluminium depends far less upon a low e. m. f. of decomposition than upon the market price of the electrolyte. The question of cost is thus more of a chemical than of an electrochemical nature. By electrolysis of a mixture of cryolite and aluminium sulphide Gin obtained aluminium sulphide in bright red crystals.

Chemical Reactions at High Temperatubes and Their Industrial Application.

A paper on this subject was presented by Zenghelis, of Athens. By burning aluminium powder in a stream of oxygen in a Hessian crucible, it was sought to obtain by chemical means a temperature equal to that of the arc light. The author estimates the temperature which he reached to be at least 4000° C. The aluminium oxide melted and partly volatilized, condensation taking place on the cold parts of the crucible. Platinum foil also volatilized. Oxide of lime and oxide of magnesium melted and partly volatilized, the remainder combining with the oxide of aluminium to form an aluminate. The excess of aluminium oxide melted to small balls, which were very hard (7½ to 8 hardness). The excess of oxygen was transformed into ozone. Presence of nitrogen and carbon gave aluminium nitride and carbide respectively. The gases H_2O, CO, CO_2, N_2O were reduced by the aluminium. NO gave nitride and oxide.

There was no discussion, but it might be here remarked that the temperature of 4000° which Zenghelis has given, but not measured, is too highly estimated. Al_2O_3 volatilizes partly in the Heraeus furnace. Platinum volatilizes when it is used to fasten the Nernst incandescent filaments; CaO always by the

preparation of carbides. The formation of the nitride also takes place at a temperature much lower than 4000°.

THE MANUFACTURE OF IRON AND STEEL IN THE ELECTRIC FURNACE.*

A paper on this subject was presented by H. GOLDSCHMIDT. He gave in a table a list of the principal electric furnace methods for the production of iron and steel, with the names of the inventors, types of furnaces, and other data. The year given is the year in which the first description was published or the patent granted.

For the German patent office Goldschmidt has recently made a test of the Stassano method and this has shown that Stassano has succeeded in preparing workably ductile kinds of iron directly from ores, with less than 0.2 per cent of C.

Stassano makes use of the very pure iron ores found in northern Italy, and which have not yet been much used. The low price of water-power in that neighborhod is also in his favor.

Comparing the efficiency of coal in metallurgical processes with electricity used for the same purpose it is seen that electricity can only successfully compete when the price of the former is high.

The heating of the charge in Stassano's furnace is performed entirely by the radiation from a powerful arc (see ELECTROCHEMICAL INDUSTRY, 1903, p. 249, Fig. 1). This is operated at about 170 volts, with an alternating current of 2000 amperes. The length of the arc, after the furnace has been some time in operation and has attained a constant temperature, is about 1 meter (3.3 feet); it operates with a loud crackling sound. The careful manner in which Stassano arranges his charges in order to get perfect reduction and a high yield is shown in a table giving the composition.*

Stassano uses mainly ores, but sometimes also waste sheet steel and raw iron. The charges are, therefore, of a mixed nature. The energy required for the reduction from ores is, of course, much greater than for melting iron for the production of steel.

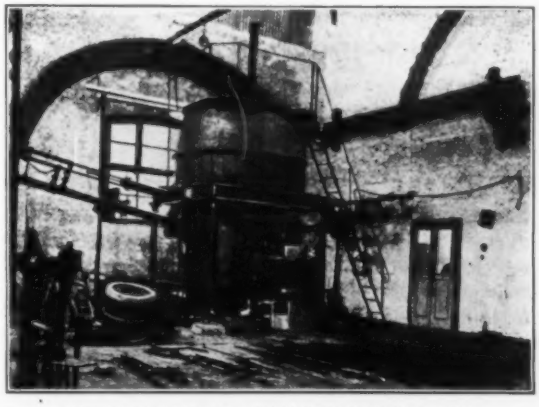
To get steel of the quality of crucible steel by means of the Stassano process, further improvements are necessary which, however, appear quite possible.

Goldschmidt then gives some figures for the Conley process and discusses at greater length the process of Keller** and Heroult.***

Keller's calculations are nearly similar to those of Stassano,

COMPARISON OF ELECTRIC FURNACE METHODS FOR PREPARATION OF STEEL BY THE ELECTRICAL METHOD.

METHOD OF	YEAR.	TYPE OF FURNACE.	MATERIAL USED.	ENERGY IN H. P. HOURS PER TON OF STEEL.	COST IN DOLLARS PER TON OF STEEL.
Gin-Leleux	1897	Furnace with carbon electrodes.	Cast iron and waste sheet iron.	----------	----------
Stassano * *	1898	Furnace with carbon electrodes, 500 H. P.	High per cent. Italian iron ore.	3800–4000	18.75
Gysinge * * * (Crucible steel quality)	1900	Furnace without carbon electrodes, 225 H. P.	Cast and wrought iron.	1320	43.00
Froges–Heroult †	1901	Furnace with carbon electrodes, 400 H. P.	Cast iron and waste sheet iron.	1200	----------
Keller † †	1901	Furnace with carbon electrodes, 1200 H. P.	Iron ore and cast iron.	3800	18.00 to 20.00
Harmet	1901	Furnace with carbon electrodes.	Iron ore.	3600	6.00 (not total price)
Schneider	1901	Furnace without carbon electrodes.		----------	----------
Ruthenburg † † †	1901	Furnace with carbon electrodes.	Iron ore.	----------	----------
Conley	1902	Furnace with carbon electrodes.	) Iron ore.) Cast iron and waste steel.	1000 1042	12.00 28.50



500 HP STASSANO FURNACE (DARFO, 1901).

and the power required for the reduction of the ore is placed at about the same figure in both cases.

For the preparation of crucible steel the electrical method

* As for some time we have given considerable space to this latest and still more or less experimental branch of electrometallurgy, the above paper by an authority of the rank of Dr. Goldschmidt, who has spent considerable thought and time for studying this matter, should be of great interest to our readers. As far as the information given by Dr. Goldschmidt has not already been published in ELECTROCHEMICAL INDUSTRY, we give his paper nearly in full. The information given by Dr. Goldschmidt on the Stassano and Kjellin processes is quite complete. Taken together with this paper, the articles published in former issues of this journal, on electrical steel processes should represent a good resume of the present condition of this branch of electrometallurgy.—ED.

** See also ELECTROCHEMICAL INDUSTRY, 1903, pages 247, 363.

*** See also ELECTROCHEMICAL INDUSTRY, 1903, page 376.

† See also the article by Heroult on another page of this issue.

†† See also ELECTROCHEMICAL INDUSTRY, 1903, page 162.

††† See also ELECTROCHEMICAL INDUSTRY, 1903, page 202.

* This table has already been published in ELECTROCHEMICAL INDUSTRY, March, 1903, page 247, table 1. It is, therefore not here repeated, nor the tables on the thermochemistry of the process, data on actual operation, and analyses of the steel produced, all of which may be found on pages 247 and 248 of our March issue. On page 247, left column, the fourth line from the bottom should read: Si-trace. In the right column, under Thermo-Chemistry, General, read CO, instead of Co_2.—ED.

** See ELECTROCHEMICAL INDUSTRY, 1903, page 162.

*** See also the article by Heroult himself on another page of this issue.

will in all probability be the most profitable. Heroult prepares in his furnace from a mixture of cast iron and steel clippings, a tool steel of best quality, which up to the present, especially in England, has found a good market.

The refined steel has the following composition:

S = 0.007 per cent.
P = 0.003 per cent.
Mn = 0.15 per cent.
Si = 0.003 per cent
C = 0.60 to 1.80 per cent.

Crucible steel of best quality is, however, also obtained according to the method of Kjellin, a Swede. The furnace (see Electrochemical Industry, 1903, p. 376) forms a transformer in which the fluid steel takes up the low-voltage secondary current with high-current density, whilst a high-pressure alternating current is led to the primary.

This method avoids the use of electrodes entirely, and is purely a smelting operation in which pure cast iron (about 25 per cent), and wrought iron are smelted together; the first may advantageously be brought into the hearth in fluid form. In its essential points this method has been worked out in the Gysinge Iron Works and appears, as also does the method of Heroult, to be technically quite satisfactory.

In the following table, an attempt is made to estimate the cost from data obtained in actual practice.

Cost of Preparation of Steel (Crucible Steel Quality) by Kjellin's Method.

Four thousand one hundred kg. steel are produced in twenty-four hours with 225 hp. (165 kw.), hence 1000 kg. require 1320 hp.-hours.

Power (the cost of 1 hp.-hour being assumed as 0.375 cent) in round numbers	$5.00
Charge	32.50
Mould	0.25
Repairs and brick work	2.08
Depreciation and interest	0.56
Wages	2.50
Total without cost of business management, license, etc.	$42.89

The cost of the charge (pure charcoal pig iron and soft iron) is taken as $32.50 per ton. A charge of specially pure materials or the addition of chromium, wolfram or molybdenum would naturally raise this item of cost considerably. The charges for repairs and brick work appear very small, indeed it is said that these would be even less if fluid cast iron and a larger furnace were employed.

A great advantage of the process seems to be in the fact that the fire gases do not come into contact with the steel, not even by diffusion. This being so, a lining of silica or magnesia stone can be employed; and finally large charges can be heated at once. The ordinary steel crucibles hold generally only 30 kg., and at most 50 kg. metal, while with the furnace at Gysinge about 1 ton can be worked. The cost of erection of a furnace, with capacity as given in the table and including electrical plant, but not source of power, is given as 15,000 crowns, Swedish. The following analyses made at Gysinge illustrate composition of various steels prepared thus:

	I.	II.	III.
Carbon	1.45%	1.20%	0.95%
Silicon	0.47%	0.74%	0.35%
Manganese	0.49%	0.46%	0.33%
Phosphorous	0.011%	0.013%	0.014%
Sulphur	0.010%	0.010%	0.015%

In the discussion which followed Danneel asked what is the difference between the furnace of Heroult and Keller. Goldschmidt replied that there are still differences regarding the patents between the two inventors. Replying further to Engelhardt, he said that the high figures of cost of the Gysinge process refer to cold charges.

Gin imparted the information that he has constructed a furnace for which he claims a high economy. The furnace is built in the form of a long canal with narrow cross section, ending on each side in steel blocks kept cool by internal circulation of water. The passage of a current of necessary strength through the conducting molten metal develops sufficient heat to keep the whole mass fluid and to impart to it the temperature most suitable for purification of the metal. The large cross section of the metal blocks at the ends of the metal canal prevents there the formation of a high temperature, and this is aided by the circulation of the cold water. In order to give the furnace a suitable form the canal is bent like the filament of an incandescent lamp.

The balance of the report will be published in our next issue.

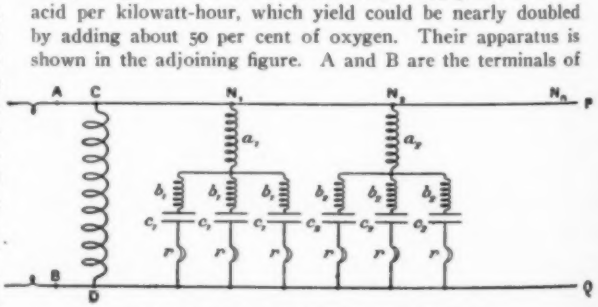
SYNOPSIS OF ARTICLES IN OTHER JOURNALS.

A Summary of Articles on Electrochemistry and Allied Subjects Appearing in American and Foreign Periodicals.

By Carl Hering.

Industrial Electrochemistry.

Production of Nitric Acid by Electric Discharges.—In a paper read before the *Société Internationale des Electriciens* at Paris, J. de Kowalski describes his method and apparatus for the production of nitrous vapors from the nitrogen of the air. He states that as early as 1899 he had observed that the yield of nitrous vapors increases considerably with the frequency of the alternating current used to produce these discharges. The experiments of MacDougall and Howles had shown that a yield of 36.6 grams of nitric acid per kilowatt resulted with a current of 0.2 ampere. Kowalski and Moscicki, working with a frequency of between 5000 and 6000 cycles per second, have obtained 43.5 grams of nitric acid per kilowatt-hour with an arc of the same intensity. They have also found that when the intensity of the current in the arc diminishes, the relative quantity of nitrous vapors increases. The length of the arc is also not without influence upon the yield. With a current of about 0.05 ampere, a difference of potential of 50,000 volts, and a frequency of 6000 to 10,000 cycles per second, they obtained a maximum of nitrous vapors for the energy employed. They have obtained 52 to 55 grams of nitric acid per kilowatt-hour, which yield could be nearly doubled by adding about 50 per cent of oxygen. Their apparatus is shown in the adjoining figure. A and B are the terminals of



NITRIC ACID BY ELECTRIC DISCHARGES.

a high-potential transformer. AP and BQ are two parallel conductors, connected by groups N_1 and N_2. Each of these groups consists of a self-induction coil *a* in series with three parallel self-induction coils *b*. Each of the latter is in series

with a condenser C and an arc *r*. The two wires AP and BQ are also connected by a large self-induction coil CD. The coil *a* is intended to prevent the oscillating discharges from reacting on the main transformer. The self-induction of this coil is calculated so that its impedance, which is very great with the high frequency currents which are produced in the charge and discharge of the condensers, shall be relatively small for the current of ordinary frequency coming from the transformer. The whole system produces a phase lead, as a compensation for which the large coil CD is arranged. The author works with a tension of 50,000 volts at the terminals of the principal transformer. One of the most important parts of the apparatus is the condenser. After experiencing considerable difficulty in this respect, they now use small glass tubes silvered on both sides. Exact measurements have demonstrated that the loss of energy in these condensers does not go above 1 per cent. The small self-induction coils for the high frequency also have to be constructed very carefully.

Electrometallurgy of Aluminium.—An article entitled *Note sur l'Electrometallurgie de l'Aluminium*, by GIN, appears in the issues of June 30 and July 15 of the *Journal de l'Electrolyse*. The author first discusses the choice of an electrolyte and lays down the conditions to which the latter has to conform. He then calculates the theoretical voltage of decomposition of a bath of aluminium fluoride, supposing that the fluorine does not escape as such, but in the form of tetrafluoride of carbon, mixed with a more carburetted fluoride. By his formula he obtains 57,450 calories and 2.49 volts, which Minet found experimentally to be 2.5 volts. For Hall and Heroult's alumina electrolyte he finds 50,650 calories and 2.19 volts. He found experimentally 2.3 volts as an average of four observations. For aluminium sulphide he finds 29,350 calories and 1.27 volts. The author concludes from these figures that for the preparation of one kilogram of aluminium from the electrolytes considered above, the energy consumed will be approximately given by one of the following formulas, in which KF, Ko and Ks are "variable quantities, between 16 and 19 kilowatts." For Al_2O_3 (KF + 8.5) kilowatt-hours; for Al_2O_3 (Ko + 7.5) kilowatt-hours; for Al_2S_3 (Ks + 4.4) kilowatt-hours. The maximum difference is therefore in the neighborhood of 5 kilowatt-hours; at the present price of electric energy, as furnished by the great water-powers, this difference represents hardly a few centimes per kilo of aluminium. In summing up the author states that the cost price of aluminium depends much less on the more or less easy decomposition of the electrolyte than on the cost of this electrolyte. The economic problem is therefore more of a chemical than of an electrochemical order. The author concludes by stating that while electrolyzing a mixture of artificial cryolite and aluminium sulphide, stopping the operation before it was finished, he observed the presence of a subsulphide of aluminium in the electrolyte, which was well crystallized and of a light cinnabar red color. He is now studying this compound.

Electrolytic Manufacture of Vanadium and Its Alloys.—A paper on this subject has been presented before the Fifth International Congress of Chemistry, at Berlin, by GUSTAVE GIN, the well-known French electrometallurgist. The principle of the process depends on the great conductivity of vanadium trioxide, and on the facility with which trifluoride of vanadium is obtained, by attacking the trioxide with fluorine in the presence of carbon. Ferrous fluoride, dissolved in molten calcium fluoride, is electrolysed with an anode composed of an intimate mixture of carbon and vanadium trioxide. The cathode is constituted by a bath of metallic iron. The fluorine is stated to attack the trioxide of vanadium at the anode, with the formation of vanadium trifluoride, which dissolves in the calcium fluoride. The fluoride is then electrolysed in its turn, which sets free metallic vanadium at the cathode. The fluorine which is liberated at the anode forms the vanadium trifluoride again. The electrodes are prepared by calcining vanadic acid in the presence of carbon, which is then mixed with a certain quantity of retort carbon and pitch, and compressed into rods in an apparatus similar to that used for the manufacture of carbon electrodes. The electrodes are kept away from air and moisture, under a layer of dry material, until they are used. The anode of the furnace is formed of a bundle of the above electrodes, and certain dispositions have to be adopted, on account of the high melting temperature of vanadium and the alloys which contain it in notable quantity. For alloys containing more than 25 per cent of vanadium, the cathode cross-section must be notably smaller than that of the anode. A good yield and a sufficiently fluid bath is obtained with an average current density of 2 amperes per sq. cm. of anode cross-section and 6 amperes per sq. cm. of cathode surface, the voltage being between 11 to 12. A certain quantity of fluorine is lost by being transformed into gaseous carbon tetrafluoride, and, therefore, there has to be, from time to time, an addition of ferrous fluoride. The iron which serves as cathode is introduced into the bath in the metallic state, a little at a time, after each cast of ferro-vanadium. If iron is not introduced into the bath, it is possible to obtain nearly pure vanadium, but the casting of the latter is very difficult, and it has to be extracted in solid form. The author hopes, also, to apply this process under the same conditions to alloys of vanadium with other metals, such as copper, aluminium, manganese, etc., wherein it suffices to replace the cathode of iron by one of the metals which are desired to be incorporated into the alloy. The paper is reprinted in *L'Eclairage Electrique*, June 27.

New Carbide Works in Switzerland.—The electrical equipment of the carbide works at Flums, Switzerland, is described and illustrated in the *Electrochemist and Metallurgist*, July, by F. C. PERKINS. The plant at the power station, which has a capacity of 2400 hp, and is situated at a distance of 1.8 kilometers from the carbide works, consists of three large turbines of the horizontal type, each directly coupled to an 800-hp revolving field alternator of the three-phase type. Polyphase current is generated at a potential of 5000 volts, with an efficiency of 93 per cent. The alternators are so dimensioned that they may also be used as single-phase machines, running also at 5000 volts. The power transmission line consists of six copper conductors insulated by porcelain and mounted on iron tops, or caps, upon wooden poles. The furnace house of the carbide plant is 30.7 meters long, 12 meters wide, and 10 meters high, the floor, roof and walls being of iron and cement, and above the furnaces is an upper deck, also constructed of iron and cement. This deck construction is extended over the whole length of the furnace room. The materials are placed in the furnaces by an electrically-operated elevator. The transformer house, which is located near the furnace room, contains three single-phase transformers, which reduce the line current from 5000 to 65 volts for use in the furnaces. The transformers are of the oil-water cooled type, of a capacity of 850 kw each. The connections to the furnaces are only 8 meters long, the secondary conductors being arranged for single-phase current from the transformers; the copper conductors have a cross-section of 4800 sq. mm. and a total weight of 4.5 tons for each group of six furnaces. Current of 2200 to 2500 amperes is employed in each furnace. The numerous carbon electrodes are regulated by hand by chain gearing. From two and a half to three hours are required to produce the carbide, and it remains another hour or an hour and a half in the furnace, in order to cool off. There are eighteen furnaces in continual operation, arranged in groups of six or of four, twelve of them being usually in operation at the same time. The carbon electrodes required, per ton of carbide produced, are said to weigh about 30 kilograms. The plant comprises, also, the usual facilities for handling and storing supplies, etc.

Industrial Electrolysis of Water.—In a recent meeting of the Société Belge d'Electriciens, M. JOTTRAND, director of the Société l'Oxhydrique, in Brussels, read a paper on the Garuti process for the industrial electrolysis of water, which is ab-

stracted, with diagrammatic illustrations, in the *Revue de l'Electricité*, July 15. The diaphragm used by Garuti is of metal, perforated by a number of holes of very small diameter, which do not allow the gas to pass, on account of capillary action. The use of such a diaphragm enables the voltage to be reduced to 2 or 2.5 volts, the metallic diaphragm not acting as intermediate electrode, if the potential does not overstep 3 volts. It is claimed that the production is 0.4 liters of hydrogen and 0.2 liters of oxygen per ampere hour, with an expenditure of 4.166 kw for a cubic meter of gas, 2-3 of hydrogen, 1-3 of oxygen. The electrolyte is a caustic soda or caustic potash solution. The gas which is obtained is stated to be very pure; the small amount of hydrogen in the oxygen is gotten rid of by passing the gas through an apparatus composed of pipes heated to a red heat, which effects the combustion of the hydrogen. The last part of the article is devoted to the description of an improved oxyhydrogen blow-pipe.

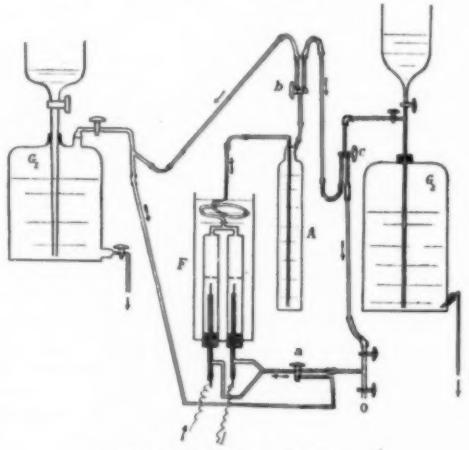
Polishing and Plating of Metals.—A long extract from a manual under this title, by Hawkins, is given in the *American Jeweler*, July. The first part deals with the question of lining tanks for electroplating purposes. Detailed instructions are given for lining the tanks with asphalt which contains a little pitch, in order to get a lining which will be thoroughly satisfactory. Particular emphasis is laid on the necessity of getting the corners well filled, by pouring in hot lining and following with a hot flat iron until the lining has melted into one solid piece; successive layers will not do, it must be one solid piece. Whether the surface is rough, as in eastern practice, where it is sanded with clean, white sand before the asphalt lining cools, or whether it is smooth, as is generally preferred in the west, makes no difference. The acid dipping jars and the jars for various pickles and dips should be arranged in a large wooden tank of shallow depth. Care should be taken not to have the waste pipes from this tank too small, as it is sometimes required to empty it very quickly, in case a pickle jar, or dip, has been upset, or in case a sudden change of work requires absolutely fresh water in the tank. In the latter case, valuable time may be lost while waiting for a 100-gallon tank to refill. The hot side of the tank should have a steam pipe open at the bottom and reaching nearly to the bottom of the tank. The steam must be clean, and should come directly from the boiler; it will not do to use exhaust steam, because it contains oil, and the rinsing water must be kept clean. The pressure must be such as to heat the water nearly to the boiling point, while a supply of cold water is constantly fed in. Much valuable time is said, by the author, to be lost by neglecting this point, as, in many places, pickling and dipping cannot begin for several hours after starting in the morning, on account of lack of steam. Detailed instructions are given in regard to arrangements of the various dipping tanks, the potash tank and the scrubbing tanks for the plating solutions, and several illustrations of such tanks are given. Solutions should be skimmed off occasionally with a suitable skimmer, to remove the dust and grease before hanging the work in the solution. Cyanide solutions will not require this very often, but nickel solutions have a tendency to form a greasy scum, which must be removed each morning before hanging in the work, in order not to cause spotty deposits, or peeling off of the work. A method is given for performing this conveniently by means of tissue paper. The extracts will be continued in subsequent issues of that journal.

The Electric Furnace.—The serial previously mentioned in the Synopsis on the electric furnace, its origin, development and forms of application, is continued by Adolphe Minet in the *Electrochem. Zeitsch.*, July and August. The types described in the July issue are the well-known Borchers type with cooled metallic cathode and two types by Willson, also well known. Then follows the description of several carbide furnaces, among which are the Bullier, Gin & Leleux, Siemens & Halske and the Willson Aluminium Company furnaces. The August issue brings, besides the furnaces types of Memmo, the well-known Parker and the Laval furnaces, a description of a new type of furnace, which is said to have been recently patented in Germany and bears the name of Neuburger-Minet. This furnace is said to be so constructed that it is possible to run it by blast-furnace gas, power gas, or electricity. It consists of a central reaction chamber, with heating chambers and regenerative chambers. The position of the electrodes varies according to the nature of the reactions and the degree of purity which is desired for the product of the furnace. If this must be free from carbon, the electrodes are situated above the central chamber. If the product can stand a certain admixture of carbon, the electrodes are brought nearer to the charge. The nature of the walls of the reaction chamber varies according to the product desired.

Production of Ozone.—In the issues of July and August of the *Electrochem. Zeitsch.*, Dr. O. Kausch continues and concludes his illustrated serial on the production of ozone by electrolysis, describing, among others, the apparatus of Tindal, Yarnold, Verley, Otto and Siemens & Halske.

Theoretical and Experimental.

Isolation of Argon from Atmospheric Air.—Two methods have been proposed for the separation of argon from the air and especially from the nitrogen of the latter, the first being the absorption of the nitrogen by chemical means, as by metallic magnesium, and, the second, the passing of electric sparks through the air, thereby converting the nitrogen into nitrous compounds. Lord Rayleigh and Ramsey used the second method, passing the sparks between two electrodes arranged inside of a large glass bulb, which was half filled with caustic soda solution and the other half of which was occupied by the mixture of atmospheric air and oxygen. This arrangement is somewhat complicated, and the danger of losing all of the



ISOLATION OF ARGON.

argon, if the glass bulb cracks, is considerable of a drawback. Another arrangement has, therefore, been elaborated by A. Becker, which permits continuous running of the apparatus and the production of any desired quantity of argon with perfect security. He describes the arrangement in the *Zeitsch. f. Electrochem.*, July 23. The apparatus is shown in the adjoining cut. G_1 and G_2 are two gasometers, filled with air and a few liters of oxygen. The air is passed from G_1 into the spark apparatus F, which consists of a vessel of sheet zinc, in the interior of which there are arranged two brass tubes of about 5 cm. diameter and 28 cm. length. The two tubes communicate at the top and lead to a lead coil, which serves as a cooler. The vessel F is filled with cold water. In the interior of each brass tube there is arranged a brass disc with a central opening, which serves as one electrode of the spark gap. This construction is for the purpose of forcing the gases into a nar-

row stream, while they are passing the spark gap. The other electrode is formed of a thick, pointed copper wire, fastened in a glass tube at the bottom. The glass tube has a side tube, through which the air is introduced into the apparatus. The terminals of the secondary of a transformer are connected with the lower ends of these copper wires. From the spark apparatus the gases pass into an absorption apparatus A, and from there into the gasometer G_2. After a certain time, the two-way cocks a, b and c are reversed and the air now travels in the opposite direction through the apparatus. The author found that the best results were gotten when long sparks were obtained and when the air passed the spark gap at a certain, exactly-determined speed, in order to avoid a recombination of the products, as well as a too rapid passage. As the absorption proceeds, fresh air, or oxygen, can be introduced at o. The cooling water in F has to be removed from time to time, but a continuous flow is not necessary. It was possible to obtain, in a few days, with two of these apparatus, two liters of gas, which, treated again by sparking, gave about 600 cc. of argon.

Decomposition of Cyanide Silver Plating Baths.—The processes which take place in cyanide silver plating baths, while they are in use, have been studied very little. The cause of the loss of cyanide, more especially, which makes a regeneration of the baths necessary after a certain time, has not been ascertained. There are, also, investigations wanting whether a bath containing silver chloride can be used. E. JORDIS and W. STRAMER tried to find out something about these questions by comparing silver baths which were running on a large scale, and published their results in the *Zeitsch. f. Electrochem.*, July 9. They experimented with three baths, one of which contained silver chloride and the two others silver cyanide. The chloride and one of the cyanide baths were used for silver plating, while the third bath was used for comparison. The authors found that the loss of cyanide and the increase in carbonate is always greater with the working bath than with the idle one. In the bath containing chloride, the loss in cyanide and the increase in carbonate was still much greater, so that the latter bath had to be regenerated oftener. This increased formation of carbonate, the authors think, can only have been brought about by an increased anodic oxidation, the causes of which are the chlorine ions. This disadvantage is offset by the advantage that the resistance is only two-thirds of that of the pure cyanide bath, and that it can, without detriment, especially without danger of sliming up the anodes, run up to a higher content of carbonate, with higher currents. It has been found that after a while more cyanide disappears than is equivalent to the amount of carbonate found; consequently, there must have been secondary reactions. The authors state that in the text books of plating there is frequently found the assertion that the products of decomposition are necessary in the silver bath to obtain a good deposit, and that new baths did not work well. It is, therefore, recommended to add a part of the old bath or potassium formate and ammonia. The authors state that this is not necessary, that the fresh bath is entirely satisfactory, if it is started with pure materials, and if the operator knows how to use a volt and ammeter.

PRIMARY AND SECONDARY BATTERIES.

The Jungner-Edison Accumulator.—The Swedish chemist, Jungner, has patented several accumulator constructions and, in the opinion of DR. M. SCHOOP, he apparently recognized, before Edison, that nickel oxide, if suitably supported upon a carrier, is a practical depolizer. The English and the German patent offices have been influenced by Jungner's objection to materially curtail Edison's patent claims. For these reasons, it seems to be more accurate to speak of a Jungner-Edison accumulator than *vice versa*. He publishes, in the *Electrotechnische Zeitschrift*, of August 6, the results of an investigation conducted with a Jungner accumulator and an ordinary lead storage battery, in order to compare their behavior during charge and discharge, their capacity, the changes of temperature and concentration of the electrolytes, and the relations between capacity and current strength. The Jungner accumulator had five negative and four positive electrodes, both formed of perforated supports of nickel-plated sheet steel, shaped like pockets, in the interior of which the active material was contained. The material of which the pockets are constructed is the same for both electrodes, but the active material is different, being nickel oxide and cadmium, or iron in a very finely divided state. Mixed with suitable liquids, they are introduced into the pockets in the form of a paste.

He summarizes his results as follows, for the lead and the Jungner accumulator: In the former, according to Faraday's law, 3.66 grams of sulphuric acid is combined or liberated, as the case may be, for each ampere hour; the solution, therefore, changes its specific gravity, its conductivity and volume. In the latter the alkaline electrolyte does not change its chemical and physical nature during any phase of the charge and discharge, and merely carries the oxygen from one electrode to the other; small amounts of liquid are, therefore, sufficient. The accumulator can be compared to an oxygen reservoir. In the lead cell, during discharge, free acid diffuses toward both sides into the pores of the plates; the concentration, therefore, decreases in the middle. In the Jungner cell, the electrolyte diffuses, during discharge, out of the pores of the nickel electrode into those of the cadmium electrode, while the density between the plates is not changed. As the active mass is present in the form of powder, and the distances between the plates can be very short, the diffusion takes place very quickly. For the good working of the lead accumulator it is necessary to adhere strictly to the average density of the acid, as given in the instruction, and to avoid a rise of temperature of the acid above a certain limit, about 40° C. The best conducting caustic solution in the Jungner cell does not conduct as well as the best conducting acid, and has the tendency to absorb CO_2 from the air. The good working of the electrodes, on the contrary, is independent within very wide limits of the concentration of the caustic solution. On the lead plate, as well as on the peroxide one, a local action takes place, which is the more violent the denser the acid is; the lead accumulator is, therefore, comparable with a water reservoir which leaks a little. The caustic solution in the Jungner cell does not seem to attack either the electrode support nor the active materials. The active materials in the lead accumulator adhere exceedingly well to the conducting support and conduct very well. The internal resistance of the lead accumulator is small and amounts to only several thousandths of an ohm, even in the smaller types. The active substances in the Jungner cell have to be brought into pockets, as they do not harden, and they have a bad conductivity. The internal resistance is two to three times as great as in the lead accumulator. The capacity in the latter is dependent upon the time intervening between charge and discharge, the temperature and density of the electrolyte, the strength of the charge and discharge current, the porosity and the thickness of the plates. Besides the quantity and structure of the active mass, the capacity is also determined by the volume of liquid present. In the Jungner cell the capacity is influenced by the strength of the discharge current to a much smaller degree, and depends chiefly on the amount of active material; the influence of the temperature of the electrolyte on the capacity is insignificant. The loss of potential, however, amounts to 35 to 40 per cent, and still more with slow discharges, while the loss of potential in the lead accumulator usually does not go above 12 per cent. The materials for the Jungner cell are expensive; a caustic solution of 30 per cent is about four times as expensive as accumulator acid; but Mr. Schoop might have added here that the volume of the caustic solution per ampere hour is, or may be, made much less, and that the total cost of the liquid is not an important part of the whole. The efficiency of the

Jungner cell is about 80 per cent in ampere hours and 65 per cent in watt hours, while the efficiency for the lead cell is, on an average, 85 to 90 per cent in ampere hours and 75 per cent in watt hours. The taller the vessel is, in the case of the lead cell, the sooner will a difference of concentration take place in the acid between the plates, by which certain local reactions are started. The space needed for the Jungner cell is about one and a half times as much as for the lead cell of about the same weight and watt-hour capacity, but there is no objection to make the height of the vessel anything desired. The author concludes that for the present the alkali accumulator has, besides the uncontested advantages just as many serious disadvantages. It must, however, not be forgotten that the lead accumulator needed twenty years to reach its present stage of technical development, and there is no reason why the alkali accumulator should be less capable of development.

Mr. Schoop's comparisons are of interest, but it should be understood that they refer only to the two particular cells which he used; the results do not necessarily apply to all alkaline cells of that type; it is not to be assumed that the alkaline cell which he used was the best that could be constructed; the results should therefore not be assumed to apply to the form made in this country by Edison, at least not until they have been confirmed for this particular cell. Moreover, such comparative figures depend on so many conditions that they may be totally different for different discharges. The only really fair comparison is to discharge each at its best normal rate, and then find the capacity in useful watt-hours per pound, and the rate in watts per pound; the weight should be the total, including everything necessary. The watt-hours efficiency and other data should then be given for those discharges. For automobile work one should not lay too much stress on the efficiency, as a cell of poor efficiency might well cost much less per ton-mile of live load over a period of five or ten years, than one of high efficiency.

Miscellaneous

Engineering Science and Chemistry.—In an interesting paper before the recent annual meeting of the German Society of Engineers, Professor W. Ostwald called attention to some problems, the solution of which is of extreme importance, and demands the closest co-operation of the engineer, and the chemist. After touching briefly on electrochemistry as an exemplification of a combination of chemistry and engineering, he remarked that just at the present time we are standing at the beginning of a fundamental change in the production of mechanical from chemical energy. This change is being brought about by the development of the internal combustion engine, which is now taking place. This seems to be another instance of the law which meets the investigator everywhere, namely, that the simplest thing always comes last. It is indeed much simpler to change the chemical energy contained in the fuel directly into mechanical energy by burning it with the necessary amount of air, than to do the same thing by means of steam as a connecting link, which process only utilizes a comparatively small part of this energy, and in which the supply of the water, its change into steam and the getting rid of the exhaust steam, are just that many sources of unnecessary complication. The question of the gasification under the best conditions obtainable with regards to the fuel under consideration, is primarily a chemical one, conditioned, however, everywhere by mechanico-technical considerations. The preponderant direction in which development will take place, is, according to Professor Ostwald, toward the establishment of large central stations, which will distribute their power either as electric current, or as gas for power purposes. He then takes up the chemical question of gasification based on the reactions $H_2O + C = H_2 + CO$ and $2H_2O + C = 2H_2 + CO_2$. The question as to how the second reaction, which does not furnish CO, could be increased, is one of chemical dynamics, and is to be answered by saying that there is practically only one possibility of doing it, namely, the lowering of the temperature. The conditions of the equilibrium are discussed, and it is shown that even the gasification of pure carbon is a complicated phenomenon, which becomes more complicated still if the water contents of the fuel, for instance, in the case of moist lignite or peat, enter into consideration. Touching now upon the question as to how the energy generated in the large power station can be distributed in a form most handy for the consumer, Professor Ostwald comes to the conclusion that electrical energy is for this purpose far superior to all other forms of energy, and that it will always be that form which best corresponds to the demand of the public, to have things in such shape that they need a minimum of care and attention. But apart from the question of gasification there are a number of great problems presented to the chemist, namely, the utilization of the by products obtained in the gasification. Attention is called to the fact that the enormous coal tar industry is based upon a consumption of coal, which does not reach the one-hundredth part of that burned under the boilers. If it is imagined that all the latter coal will be gasified, the perspective of the tremendous amount of the by products to be dealt with, and the accompanying possibilities is bewildering. The ammonia also, which is formed from the nitrogen in the coal, will play an important role in agriculture. Professor Ostwald mentioned the fact that he has lately succeeded, with the help of his assistant, Dr. Brauer, to convert ammonia quantitatively into nitric acid, which process could be carried out on a large scale. This reaction, up to the present, could only be performed quantitatively as a lecture experiment. Reviewing his preceding remarks he calls attention again to the necessity of co-operation, as neither the engineer nor the chemist alone will be able to do justice to the demands of the problem. The paper is reprinted in the *Zeitsch. f. Calcium-Carbid Fabrication*, July 10 and 17.

ANALYSIS OF CURRENT ELECTROCHEMICAL PATENTS.

By George P. Scholl, Ph. D.

Electric Furnaces and Furnace Products.

Process of Smelting Metals and Metal Compounds. G. Egly, Charlottenburg, Germany. Patent 733,578, July 14, 1903. Application filed Jan. 14, 1903.

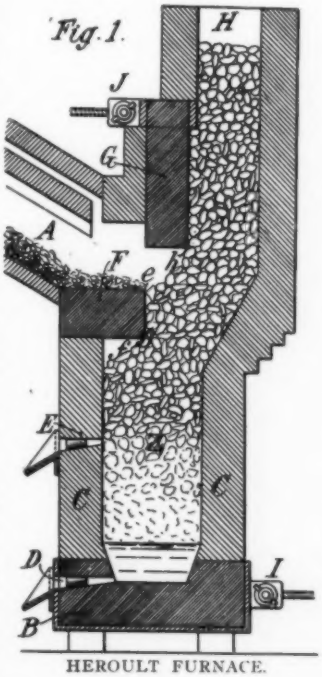
The purpose of the invention is to prevent metals reduced in the electric furnace from taking up carbon from the electrodes, thereby diminishing their value. The means proposed for the prevention of this is the formation of a slag or scoria, which is to be arranged on top of the lower electrode so as to prevent the molten material from coming into contact with it. The slag or scoria is to be composed of a substance which, though a good conductor of electricity, is chemically undecomposable to as high a degree as possible, and, furthermore, in the presence of carbon and metals, will not melt or will only melt with difficulty. The invention is to be applied especially to the reduction of nickel from its oxide. The inventor states that magnesia is a material especially well fitted for the formation of such a scoria, as it is in remarkable degree indifferent to

high temperatures. To the magnesia is added a substance which conducts electricity in the cold or at red heat, and which is chemically inert, non-volatile and undecomposable at the high temperatures to which it will be subjected. As examples of such substances are cited fluorspar, titanium dioxide, titanium monoxide and the like. These substances are added to the magnesia in the proportion of about 20 to 25 per cent by weight. The apparatus shown in the specification in which the melting process is to be carried out, has the shape of an ordinary melting pot of fire clay, the bottom of which is formed of an electrode. The latter is covered by a layer of the scoria, and on top of this is a layer of molten metal. A second layer of slag formed in the operation of melting separates the other electrode, which is represented as a rod, from the metal. After the lower electrode, which in the case of direct currents is the cathode, is covered by a scoria of the nature described, it is allowed to cool to a red heat and then the reduction of nickel is carried out preferably by direct current of low density. The current density employed is stated to be preferably about 2 amperes per square centimeter, although good results may be obtained at lower current densities. The process may also be used for the smelting of metals, for instance, of nickel or wrought iron waste from which cast steel is to be manufactured. In this case so much scorifying material is to be added to the metal to be smelted that a covering scoria will be formed in a short time.

Electric Furnace. P. L. T. Heroult, La Praz, France. Patent 733,040, July 7, 1903. Application filed March 27, 1902.

The principle of this latest furnace construction of the well-known electrometallurgist depends upon the treatment of ores which have been previously fused until they have reached a pasty condition or are sufficiently softened to descend progressively into the furnace. The furnace is not intended to operate alone, but works in connection with another. It is illustrated in the adjoining Fig. 1. The furnace consists of a carbon crucible B, surmounted by a well C, which has walls of refractory material. Openings are provided at D and E, the upper one serving as a slag hole and the lower one as tapping hole. The reduction of the ores takes place in this well, which contains a high column of coke or other fuel through which the current passes. The ore enters into the furnace by the passage A, leading from the furnace in which it has been previously brought to a pasty condition. This pasty mass becomes mixed with the descending column of coke and is reduced on its way down to the bottom of the crucible. As the carbon disappears in reducing the ore, the coke column is fed at the top from a reserve contained in the upper part of the furnace. The fuel which causes reduction of the ore, and which really forms one of the electrodes of the furnace, therefore flows into the furnace in a continuous manner as the operation goes on. On top of one of the walls of the well C is placed a block F of carbon, which forms the floor of the preparatory furnace mentioned above; by its means the ore is delivered right into the middle of the coke column. The block is so arranged that it can be easily replaced when it is worn out. Another carbon block G, of variable form, is arranged so as to constitute one of the walls of the upper structure H, through which the fuel is introduced. The terminals of the supply circuit are connected to the crucible by means of the connection I and to the block G by means of the connection J. The block or so-called false electrode F establishes a short circuit, with the block G through that portion of the carbon column which is above the well, so that the two points *e* and *f* are at intense heat. It is stated that owing to this intense heat, the floor which the block F forms, is cleared from the fused or pasty ore so that there can be no accumulation of ore which might obstruct the column. On the other hand at *h*, there is obtained a high temperature which superheats the descending carbon. The gases escaping from the reduction of the ore pass through the passage A into the preparatory furnace. The upper carbon blocks are stated to seldom require to be replaced if they are shielded from the air, a condition which is fulfilled, as they are always surrounded by the gases resulting from the reduction of the ore. The furnace described is stated to be especially suited to the production of cast iron, ferro silicon, ferro manganese and other like products.

Fig. 1.



HEROULT FURNACE.

Process of Removing Silica From Coke. Charles M. Hall, Niagara Falls. Patent 733,389, July 14, 1903. Application filed Sept. 24, 1902.

In this specification Mr. Hall outlines his method for the treatment of the carbon electrodes which are to be used in the manufacture of aluminium. For this purpose they should be substantially free from silicon, as the latter element is taken up by the aluminium and spoils its quality. The process consists, broadly stated, in mixing with the carbonaceous material to be treated a metallic fluoride, for the purpose of forming with the silicon contained in the material a gaseous fluoride of silicon, which will go off during the baking. A number of different fluorides have been used, sodium fluoride, cryolite and fluorspar giving good results. The coke to be treated is first pulverized, and mixed with sufficient sodium fluoride to remove all, or the greater part of the silicon as silicon fluoride. The material is then mixed with a suitable binder and formed into blocks or any other desired shape, and subjected to a baking process in an electric furnace. The latter contains a core of any suitable material adopted to be raised to a regulated temperature by preferably an alternating current. The articles are insulated from each other while they are being baked. One of the materials thus treated was Pocahontas coke, with 4.4 per cent ash. The principal constituents of the latter were as follows: SiO_2, 44.98 per cent; Fe_2O_3, 14.53 per cent; Al_2O_3, 28.27 per cent; CaO, 3.45 per cent; TiO_2, 3.51 per cent; Na_2O, 2.25 per cent, with small quantities of manganese and magnesium oxides. One hundred and thirty parts by weight of this coke were mixed with 60 parts of hard pitch, 7 parts of tar and 10 parts of sodium fluoride, after which the mixture was thoroughly baked, having been previously formed into blocks. The carbons were then examined, and it was found that the ash had been reduced from 4.4 per cent of the total weight to 3.51 per cent. Of this latter the titanium dioxide was reduced to 3.31 per cent, and the sodium oxide was increased to 13.78 per cent; but at the same time the silica was reduced to 18.32 per cent, or less than one-half the amount in the coke before it was treated. The carbons were thus well adapted for use in electrolysis. Instead of mixing the coke, fluoride and pitch and forming them into the desired shape before baking, in this way combining the purification and the preparation of the electrodes in one process, the purifying steps may be carried out separately by heating the mixture of coke and fluoride alone.

APPARATUS AND PROCESSES FOR THE ELECTROLYTIC PRODUCTION OF METALS AND COMPOUNDS.

Apparatus for the Electrolytic Decomposition of Alkali Chlo-

rides. C. Fournier, Geneva, Switzerland. Patent 734,312, July 21, 1903. Application filed June 25, 1902.

The specification describes an apparatus for the electrolysis of alkaline chlorides, which belong to the diaphragm type of apparatus, having even two diaphragms instead of one, as the inventor proposes to use a middle compartment. The inventor refers first at length to the various disadvantages encountered in such apparatus where pressure is used on the middle compartment in order to prevent the products of electrolysis in the anode and cathode compartment from reacting upon each other. He then states that the novel feature of his invention is based in the fact that caustic soda is considerably more soluble in the solution of chloride of sodium than the chlorine. It is, therefore, neither necessary nor advisable to exert an equally great pressure by means of the central liquid on the anode and cathode liquids. Further, it is claimed to have been shown by experiments that very little chlorine passes through the diaphragm if the pressure of the liquid is equally great on both sides of the porous partition between the anode and the central cell. But it is proposed to even destroy this small quantity of chlorine at the moment of its passage through the diaphragm by an arrangement by which a quantity of caustic soda, exactly corresponding to the small quantity of chlorine is directed against it, and further by heating the electrolyte which lies between the two diaphragms to a sufficiently high temperature. These two precautions are evidently not enough to destroy that very small amount of chlorine, and, therefore, the inventor takes still a further precaution, namely, that of adding a certain amount of ligh metallic oxide, more particularly cobalt superoxide to the electrolyte in the middle compartment. It seems as though in spite of the pressure on the central compartment there was soda diffusing into the middle compartment from the cathode side and chlorine from the anode side, for they are expected to form sodium hypochlorite in the middle compartment, which it is the function of the cobalt superoxide to reconvert into NaCl + O. The apparatus with its accessories, in which this process is to be carried out, is represented in Fig. 2. It consists of an electrolytic cell which is divided into three compartments, the anode cell *a*, the intermediate compartment *m*, and the cathode compartment *k*, which is subdivided into three parts again. An anode *t* of carbon is arranged in the anode compartment, the material of the cathode is not mentioned, but it appears from the sketch as though a plate of iron were intended to be used, as only one connection is shown for the three superimposed cathode cells. The three cathode compartments are arranged in such a manner that the upper one receives the fresh chloride of sodium solution through pipe *h*, while it delivers a solution already somewhat charged with

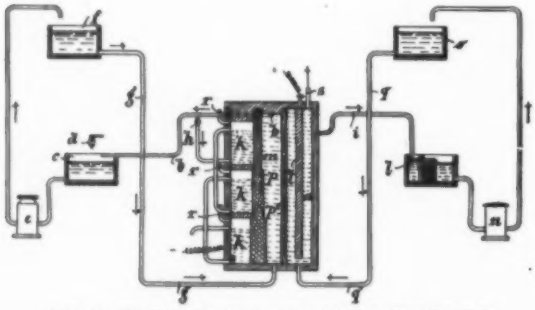


FIG. 2.—ELECTROLYSIS OF ALKALI CHLORIDE.

alkali into the middle cathode compartment, where it is still further enriched before passing into the lowest part. From there it is drawn off for further treatment. Hydrogen is stated to escape by pipes *r*, *r*, *r*. According to the increasing contents of alkali in the three compartments of the cathode side of the apparatus, the porous wall of the middle compartment toward the cathode is also made in three thicknesses, being thickest in the lower part. *s* in the anode compartment is supposed to be a pipe leading off the chlorine, though what prevents the solution from spurting out there under the conditions illustrated is hard to see. The middle compartment solution which has become cold in the apparatus, passes out through pipe *b* into a tank *c*, where it is replenished if necessary through valve *d*. From there it runs through a heating apparatus *e*, whence it is lifted to a feed tank f, arranged at a height determined according to the degre of hydraulic pressure it is intended to carry. The solution returns again to the middle compartment by means of pipe *g*. From the anode compartment a pipe *i* leads to a tank *l* in which the salt contents of the solution are automatically replaced. The solution then flows into a lifting device, which elevates it to the feed tank *o*, whence it is returned to the anode compartment. Cobalt superoxide, as stated above, is introduced into the middle compartment, preferably by saturating pieces of pumice with nitrate of cobalt, then rendering them incandescent, and after that packing them loosely into the middle cell. An apparatus like the above, with its many complications, is hardly likely to prove a serious competitor to the simple mercury processes.

Manufacture of Peroxide of Lead. E. Querenfeldt, Duisburg, Germany, Assignor to Chemische Fabrik Griesheim Electron, Frankfort, Germany. Patent 734,950, July 28, 1903. Application filed June 25, 1901.

The invention relates to a process for the direct conversion of lead oxide (litharge, red lead and the like) into lead dioxide. This conversion is effected by subjecting to electrolysis an emulsion of lead oxide with a concentrated solution of an alkaline chloride or the chloride of an alkaline earth. Electrolysis is carried out at a pressure of about 3 volts, and a corresponding current intensity, the anode being of platinum carbon and the like, and the cathode of any metal. The latter is preferably fitted into a frame over which parchment paper or another suitable material is stretched, in order to separate it from the anode. No trace of chlorine is stated to be evolved at the anode, while hydrogen is given off at the cathode. The lead oxide is kept in constant motion, and under the influence of the current gradually becomes brown, and towards the end of the electrolytic process black-brown. The conversion is stated to take place quantitatively in the time calculated from the current intensity required for the oxidation. The inventor thinks that as lead oxide is but very imperfectly oxidized by hypochlorous salts, it is to be supposed that the hypochlorite formed during electrolysis does not act directly on the lead oxide in the emulsion, but on the compound of alkali and lead, $Pb\begin{matrix}ONa\\ONa\end{matrix}$, which must be formed as an intermediary product and pass into solution. The latter presents an advantage in so far as it is not necessary to effect a preliminary solution of the lead oxide in hydrochloric or acetic acid. The alkali which is always present in small quantities in the electrolytic process will dissolve corresponding quantities of the compound of alkali and lead, which are at once converted into lead dioxide and alkaline chloride by the hypochlorite or chlorine, according to the reaction $Pb\begin{matrix}ONaCl\\ONa\end{matrix} + Cl = PbO_2 + 2\ NaCl$. The peroxide being formed in a state of emulsion, assumes a pulverulent form. The process is conducted in an earthen vessel, placed in a water bath, which is heated by a steam coil, and a stirring device keeps the emulsion in constant motion.

Electrolytic Manufacture of Chlorates and Perchlorates. P. Lederlin, Chedde, France. Patent 732,753, July 7, 1903. Application filed July 11, 1902.

The present invention relates to an improvement in the manufacture of chlorates and perchlorates by electrolysis, in order to obtain a high yield of the current. The inventor claims to have discovered that the addition of a chromate or bichromate to the electrolyte can be dispensed with, if care is taken that the liquid is kept non-alkaline by convenient additions of dilute hydrochloric acid. He states that by making these addi-

tions, it is easy to obtain a yield, for instance, in chlorate of sodium of from 0.50 to 0.55 grams per ampere-hour. By making the additions continually a yield of 0.58 to 0.61 grams per ampere-hour is obtained, which corresponds to 90 per cent of the theoretical result. The chlorate is obtained periodically from the liquid by refrigeration and crystallization, and the solution replenished with fresh chloride. The precise amounts of hydrochloric acid which it is proposed to add to the electrolyte are not stated in the specification.

Electrolytic Apparatus for Recovering Metals From Their Compounds. C. E. Baker and A. W. Burtwell, Cleveland, Ohio. Patent 734,499, July 28, 1903. Application filed Nov. 11, 1902.

The apparatus is based upon the use of metallic mercury, an absorbent for the metals to be recovered, and is more especially to be employed for the production of metallic sodium and chlorine from sodium chloride solution. The apparatus is illustrated in Fig. 3. A vessel of sheet iron 5 is provided with a cement lining 6 and filled with a solution of sodium chloride, for which inlet pipes 8 and outlet pipes 7 are provided. Carbon electrodes 11 serve as anodes, and pipe 10 is intended to carry away the chlorine. Metallic mercury 12 covers the bottom of the apparatus and flows by means of pipes 13 and 15 into two retorts 2, which have outlets 17 and are heated by Bunsen burners 16. The mercury is vaporized in these retorts, and passes through pipes 18 and 19 into a condensing worm 3, whence it returns to the bottom of the apparatus. Pipe 13 is introduced into the apparatus through an insulating bushing 14.

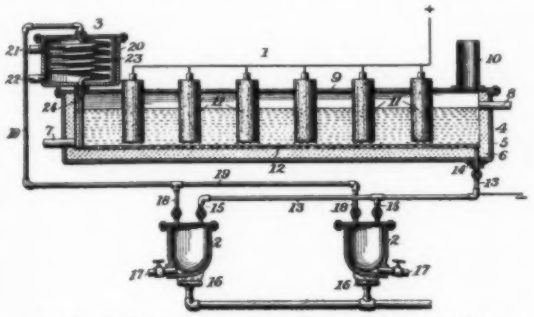


FIG. 3.—PRODUCTION OF SODIUM FROM SODIUM CHLORIDE.

and is connected with the negative source of the current, thus making the mercury the cathode of the apparatus. The metal which was amalgamated with the mercury, f. i. metallic sodium, remains in the retorts and is removed through outlet 17, or otherwise. The inventors have evidently lost sight of the fact that they have to retort enormous quantities of mercury in order to get a little sodium. It is not possible to keep the amalgam under the influence of the current long enough to enrich it to any considerable extent, as it cannot be kept from reacting with the electrolyte, and thus forming disturbing compounds with their attendant disadvantages on the electrolysis of the sodium chloride. Besides that it is hard to see how they can get the scum of amalgam on the surface of the mercury down into the little pipe which leads to the retorts.

Basket for Holding Tin Scraps. M. Laernoes and John Dunn, Streator, Ill. Patent 734,894, July 28, 1903. Application filed Nov. 25, 1902.

The specification describes an improved construction of such a basket, especial attention being paid to making it strong and durable. The basket is made of perforated sheet metal, reinforced at the corners by angle-irons. The latter are extended over the side walls of the basket in the form of yokes, and provided with laterally extending handles, by which the basket is supported in the electrolyte, as they rest on the sides of the electrolytic vessel. One handle serves as conductor of the current and makes contact with a conducting rail arranged on one side of the electrolytic box. Between the shank of the handle and the upper ends of the yoke there are interposed layers of tin or tin foil, which serve as fuse, in case a current of greater strength than desired passes through the electrolyte. Another layer of tin foil is placed between the handle and the current-conductor rail.

Metal Anode. H. E. Starrett, Chicago, Assignor to the Hanson & Van Winkle Co. Patent 733,602, July 14, 1903. Application filed Dec. 19, 1901.

The anode described in the specification is of elliptical cross section, in order to insure an even disposition of metal on the cathode opposed to such anode, and to overcome the well-known tendency of the deposit to become thicker at the edges. Another object of the invention is to provide frequent passages between adjacent anodes for the circulation of the electrolyte, and to get the anode free from sharp angles and corners at the edges. The inventor has found in practice that such an anode having a cross section of elliptical form, f. e. having a long diameter two or three times its shorter diameter, is best for the average plating bath.

Electrolytically Coating Iron with Zinc. E. Goldberg, Moscow, Russia. Patent 733,028, July 7, 1903. Application filed April 17, 1902.

The invention consists in adding to the electrolyte in which the iron is to be plated, a compound containing nitrogen in combination with an organic radical. Suitable compounds for the invention are the amines, amides, cyanides, nitrites or like compounds in which the nitrogen is attached directly or indirectly to an organic radical. The pyridene bases are stated to have given the best results. The process is carried out in the following manner. The electrolyte consists of a solution of 10 grams of zinc chloride and 10 cc. of pyridene to one liter of water. Enough hydrochloric acid is added to dissolve the double salt of zinc chloride and pyridene which is formed. A current not exceeding 0.2 amperes per square decimeter is required. Zinc is used as anode and the object to be coated with iron as the cathode. It is stated that a pure white, dense and bright deposit of zinc is obtained in this manner.

Process of Nickel Plating. T. A. Edison, Llewellyn Park, N. J. Patent 734,522, July 28, 1903. Application filed Feb. 14, 1902.

The object of the process is to produce an adherent coating of nickel on iron or steel surfaces, and it is applicable to sheets or other forms which are subsequently drawn, stamped or pressed, or to articles which already have their ultimate shape. The articles of iron or steel to be plated, are first covered in an ordinary nickel-plating bath, with a thin coat of nickel. They are then stacked together, and introduced into a cast-iron chamber or clay retort, in which a non-oxidizing atmosphere is produced by passing through an inert gas, preferably hydrogen. While the current of gas is passing the articles are heated to a bright yellow heat, which is said to be sufficient to weld the thin covering of nickel to the iron or steel backing, so that the film will not crack or flake off during the subsequent mechanical treatment to which the articles are subjected. The passage of the inert gas is continued until the articles have cooled down below the point of oxidation. It is claimed that nickel articles can be produced in this way more cheaply than the tinned ware, as the coating of nickel on the former is very much thinner than the coating of tin on the latter.

STORAGE BATTERIES.

Secondary Battery. W. Gardiner, Chicago, Ill. Patent 732,842, July 7, 1903. Application filed Jan. 23, 1902.

The battery consists of an outer tray, rectangular and relatively shallow, of iron, copper or other suitable metal, the bottom of which is covered with copper wire gauze. Upon the bottom thus formed are placed a number of longitudinal and transverse insulating strips of hard rubber, which also extend up the sides of the tray. A second tray similar in shape to the first, rests upon these insulating strips. This inner receptacle may be made of copper and plated with silver or other suitable material and is provided on its bottom with a network of

wires, which may be of silver or silver plated. This inner receptacle is filled with active material, in a relatively hard, but porous form, consisting of relatively pure silver thoroughly mixed with mercury and molded to the desired form. When the elements of each cell are assembled in this manner the cell is closed by a sheet of the same metal as that of the outer tray, and the cover soldered on. The electrolytic fluid may now be poured in through an aperture left in the outer tray for that purpose. The electrolyte preferably used consists of a strong solution of zinc oxide and an alkali, such as potassium or sodium hydrate. The outer tray, with its lining of wire gauze serves as the negative electrode, and the inner tray with its active material is the positive electrode. In charging the cells, zinc is liberated and deposited in the outer cell on the wire gauze, while the oxygen set free is said to be combined and included in the active material in the inner tray.

Method of Preparing Electrolytes. W. Gardiner, Chicago. Patent 732,843, July 7, 1903. Application filed Jan. 23, 1902.

The specification describes a method of preparing the electrolyte in that form of storage batteries, in which the electrolyte is formed of a solution of oxide of zinc in sodium or potassium hydroxide. The usual manner of preparing this electrolyte consists in the solution of zinc oxide in a solution of sodium or potassium hydrate, but as the latter is only capable of dissolving a comparatively small quantity of zinc oxide, it is necessary to employ a large volume of solution for a given capacity of the cell. The inventor's method consists in dissolving oxide of zinc, made by the wet process in a strong solution, preferably of caustic potash. This solution is then placed in a cell having suitable electrodes, and electrolyzed until the greater portion of the zinc contained in it is deposited upon the positive electrode. The solution is then removed and a second quantity of oxide of zinc dissolved in it, after which it is replaced in the cell and electrolyzed again, until the zinc has been deposited as before. This process may be repeated until sufficient zinc to equal the capacity of the desired battery is deposited upon the positive electrode. The solution used to dissolve the oxide of zinc may then be removed and a strong fresh solution of pure caustic potash and water, containing no zinc oxide, may be substituted. The battery is then ready for charge and discharge in the performance of work. During the discharge the zinc accumulated upon the electrode in the prior charges upon the positive electrode dissolves or is taken up in the solution, so that after the discharge is completed a far greater quantity of zinc is dissolved or contained in the solution than could be possible by the old process. It is stated that a cell of this character may be charged very much quicker than an ordinary cell of its kind, inasmuch as the electrolyte contains a great excess of zinc, which is held in solution in an unstable condition and which is therefore deposited almost immediately when the charging current is applied. The method is evidently intended to furnish an electrolyte for the cell constructed by the same inventor, which is described above.

Active Material for Electric Accumulators. Alida L. Rosenthal, Administratrix of S. A. Rosenthal, deceased, London, England. Patent 733,918, July 14, 1903. Application filed May 8, 1903.

The invention consists in the employment of urea sulphate, $(CO(NH_2)_2)\ 2H_2SO_4$ as a binding agent for the active material of electric accumulator plates where the oxides of lead, finely powdered—such as, for example, litharge, minium or red lead, but preferably litharge—are used. The invention also comprises the process of manufacturing and the employment of a small quantity of lead sulphate in combination with the urea sulphate. It is claimed to have been shown by experiments that in employing a solution of urea sulphate in water of suitable strength, and by mixing this solution with the finely powdered lead oxide, an extraordinary hardening effect is produced upon the combination. In order to prevent a too rapid hardening and to allow the molding into the desired form, the urea sulphate solution is first mixed with dilute sulphuric acid, preferably of 1.2 specific gravity. This mixed solution is then incorporated with the lead oxide until a stiff paste is obtained, which is compressed or molded into the desired form. After the paste plate has set, a frame of lead may be cast around it to complete the electrode, or it may be filled into a lead grid in the form of stiff paste. One and one-half parts of urea sulphate to four to six parts of water, with an addition of 5 per cent of lead sulphate, has yielded a suitable solution. One part by volume of this solution is mixed with one and a half to two parts by volume of a solution of sulphuric acid of 1.2 specific gravity. It is stated that when the pasted plates are formed by the usual electrolytic action, the paste becomes very coherent, and has a hard and toughened texture and surface, and that on this account a battery formed with these plates has been found to be specially adapted for use for electric traction, electric cars, and such purposes where a high discharge output and durability are required.

Galvanic Elements.

Zinc Cup for Primary Batteries. V. G. Apple, Dayton, O. Patent No. 731,422, June 23, 1903. Application filed March 23, 1903.

The invention is designed to overcome some of the ill effects due to the employment of zinc cups for portable, and more especially dry batteries, which cups are made of rolled sheet zinc, bent into cylindrical form and soldered together. The rolling of the zinc sheets hardens the surface and prevents the proper action of the exciting fluid on the zinc, and local action is set up at the joints where the solder is employed, owing to the presence of two dissimilar metals. The inventor now proposes to cast the zinc into molds, and in order to overcome the tendency of cast zinc to show blow holes, he performs the casting operation under pressure. The zinc is heated up to its melting point (about 420 degrees) and cast under a pressure of 125 pounds to the square inch. The inventor prefers a corrugated form of cup, thus providing a maximum of active surface in the interior of the cup, and at the same time getting the cup somewhat yielding, so as to permit expansion and contraction of the liquid contained in it.

Miscellaneous.

Process of Preserving Beer. F. Crotte, New York. Patent 734,305, July 21, 1903. Application filed Jan. 19, 1900.

The inventor states that the principle of this process consists in the application of the cataphoric action of the electric current. He fills a long tube, which is preferably made of copper, silvered externally, with an antiseptic, such as boric acid or the U. S. P. standard solution of peroxide of iron or other preservative, either solid or in solution. This tube is then introduced into the barrel containing the beer which is to be preserved. It is provided with a knob at the bottom and is connected with one of the poles of a powerful spark coil. Its length is such that it reaches nearly to the bottom of the barrel. Opposite this long tube on the outside of the barrel, there is arranged the other electrode, also preferably of copper and provided with a knob. A sponge soaked with water or the same antiseptic solution as that contained in the tube may or may not be in contact with the second electrode. The connections are so made that the tube forms the positive electrode and the inventor claims that when the circuit is in such condition that the silent or brush discharge passes between the electrodes, cataphoric action will result, the effect of the high-tension current being to convey the preservative substance in the tube in infinitesimal quantities through the tube wall into the beer. The current is passed through the beer for a period of from five to ten minutes. In order to further insure the destruction of the organic life in the beer, it is stated to be preferable to supplement the passage of the high-tension current by passing a current of low tension—100 to 110 volts—through the beer for five to ten minutes.

CURRENT NOTES.

DREXEL INSTITUTE.—We have received from the Drexel Institute, of Philadelphia, a circular concerning their reorganized School of Electrical and Mechanical Engineering. The two courses, one in electrical and one in mechanical enginering, are separate, and each is of two years' duration. The subjects of instruction in the first year are the same for both courses. They include higher mathematics, advanced physics, technical chemistry, and most of the distinctively engineering subjects which are pursued in common by the two classes of students. At the beginning of the second year the student makes a choice between the two branches of engineering, and thereafter devotes his time to the special work—electrical or mechanical—which he has elected. For admission a good high school or equivalent education is required. The tuition fee is $75 per year.

AMERICAN ELECTROCHEMICAL SOCIETY.—At the meeting of the Board of Directors of the American Electrochemical Society, held at Philadelphia on August 7, the following gentlemen were elected members of the Society: George M. McKee, Hinckley, N. Y.; W. J. Hammer, New York; J. A. Macdonald, Philadelphia, Pa.; F. A. Lidbury, Niagara Falls, N. Y. The names of the following gentlemen will come up for election at the September meeting of the Board of Directors: M. L. Davies, Bay City, Mich.; Charles M. Perry, Pawtucket, R. I.; T. E. True, Elizabeth, N. J.; Thomas B. Stillman, Hoboken, N. J.; L. M. Dennis, Ithaca, N. Y.; Alan A. Claflin, Littleton, Mass.; Heyward Scudder, Boston, Mass.; J. H. Beal, Scio, Ohio; Ernst Fahrig, Philadelphia, Pa.; J. G. White, New York; Anthony F. Gref, New York; Carl C. Curtis, Sandusky, Ohio; Wilson G. Howell, New York; W. R. C. Corson, Hartford, Conn.; Louis Duncan, Boston, Mass,; Ervin Dryer, Chicago, Ill.; C. D. Brown, Windsor, Conn.; James A. Wotton, Atlanta, Ga.; J. L. Merrill, Pittsburg, Pa.; M. W. Hanks, Pittsburg, Pa.; J. M Kent, Kansas City, Mo.; E. A. Sjoestedt, Sault Ste. Marie, Ont., Canada; H. N. McCoy, Chicago, Ill.; E. H. Clapp, Boson, Mass.; George T. Scholl, Philadelphia, Pa.; Franz Meyer, New York; Alonzo C. Bell, New York; Stephen Gardner, Chicago, Ill.; Edmund O. Schweitzer, Chicago, Ill.; H. B. Smith, Worcester, Mass.; G. C. Rowe, Havana, Cuba; Hamilton Wingate, Forest Hill, London, England; Wilber T. Earl, Niagara Falls, N. Y.; George W. Bauer, San Francisco, Cal.; Shigekan Tadu, New York; R. T. Conger, Pittsfield, Mass.; H. S. Wilson, Pueblo, Mexico; Ernest B. Le Mare, Manchester, England.

THE EFFECT OF IMPURITIES IN SALT IN MERCURY CATHODE PROCESSES.—The third volume of the Transactions of the American Electrochemical Society contains an interesting paper by Dr. J. Wallace Walker, and Charles S. Paterson, on "The Influence of Some Impurities in Salt Upon the Yield of Caustic Soda by the Amalgam Process." As this paper has been read by title, and was therefore not abstracted in our report of the meeting, a brief account of it should be of interest here. With chemically pure sodium chloride the loss (as represented by the amount of hydrogen evolved at the mercury cathode) is constant, about 1.5 per cent, so that the yield of caustic soda is almost theoretical. If a single impurity like K, Ca, Mg or Fe is added to pure sodium chloride, the loss remains small, except in the case that the single impurities are Ni or Co, which cause considerable loss; but as these are not generally found in commercial salt, this is of no great industrial importance. The most important fact brought out by the investigation is that the addition of an extremely small amount of Fe to commercial salt, already containing traces of calcium and magnesium, is sufficient to cause a loss of as much as 30 per cent, and that this loss does not increase much with the concentration of iron. Another observation made is that the amalgam formed, when chemically pure salt is used, shows no immediate signs of decomposition in the cell when the current is turned off; when iron is present in the salt, however, decomposition is immediately noticeable. The principal result of importance for practice is that with a salt containing small quantities of the impurities common to natural salt, such as calcium, magnesium or potassium, the loss in the amalgam process will be very small. If, however, in addition to these, the cell should become contaminated with the minutest traces of iron salts, such as might be produced by the action of the chlorine on any iron or iron compounds in the apparatus, the effect may become so great as to render the plant useless.

CORRESPONDENCE.

PROF. HABER'S REPORT ON ELECTROCHEMISTR IN THE UNITED STATES.

To the Editor of ELECTROCHEMICAL INDUSTRY.

Sir—Permit me to say a few words in reply to some criticism on my report, printed in the July number of ELECTROCHEMICAL INDUSTRY.

Mr. Charles S. Bradley considers my account of the work of the Atmospheric Products Co. as of the kind that "tends to injure the commercial development." I have never, in anything I have published, had such a thought, and I do not see how such construction can be placed on my impartial remarks on the Atmospheric Products Co. I very highly appreciate the great success of this company in the production of nitrous fumes from air, and I have emphasized my admiration for their work in my report. The result of the work of the company in transforming the nitrous fumes into strong nitric acid is, however, still unknown to me; but should Mr. Bradley convince me of his success in this respect, none will be more glad than myself to acknowledge the very high merit of the commercial value of the process.

Dr. Joseph W. Richards protests against my comparison of the system of education in American and in German universities. In my report I referred to the fact that my view agrees with that of prominent professors in American universities—H. Muensterberg, E. D. Perry—and I can point to the notes of Dr. Theodore W. Richards and Dr. Alexander Smith, which are published, with that of Dr. Joseph W. Richards, in the July number of your journal.

Dr. J. W. Richards thinks that what I have said may be valid for those universities which I visited, but I should not have generalized. While in the United States I visited the following universities: Harvard, Johns Hopkins, Cornell, Leland Stanford, Universities of Michigan, of Wisconsin, of Chicago, of California, of Pennsylvania, the Case School of Applied Science, and the Massachusetts Institute of Technology.

I should think that a view based on a visit of these twelve institutions justified some generalization. Moreover, the two general features which Dr. J. W. Richards mentions, "the low entrance requirements, and the low plan of undergraduate instruction," became evident to me, not only from my visit to the universities, but from conversations with colleagues, and from the publications of the universities I have collected, which report these facts.

I therefore think that my esteemed colleague, Dr. Joseph W. Richards, will not consider it unfair if I say on my part, that to me it seems that he practices in some regards "the scientific use of imagination" to fill up gaps in his knowledge concerning my information, and sometimes with results far from the truth.

F. HABER.

KARLSRUHE, GERMANY.

BOOK REVIEWS.

ANALYSIS, DETECTION AND COMMERCIAL VALUE OF THE RARE METALS. By J. Ohly, Ph. D. Denver: Industrial Printing and Publishing Company, 1903. 216 pages. Price, $3.00.

The plan of this book is to take up each of the rare metals separately, and to give for each its history, chemistry and commercial aspects, mineralogy, detection, qualitative determination and quantitative estimation. Following out this plan, the

book contains twenty-nine chapters, devoted to the following twenty-nine elements: Tungsten (wolfram), niobium (columbium), thallium, tantalum, molybdenum, tellurium, platinum and the platinum metals, palladium, rhodium, osmium, ruthenium, iridium, selenium, germanium, uranium, indium, gallium, vanadium, beryllium (glucinum), thorium, zirconium, cerium, lanthanum, ytterbium, scandium, titanium, lithium, cæsium, rubidium. The chapters average a little over six pages each, although tungsten has eight pages, molybdenum eight, uranium ten, and vanadium thirteen.

Following these are a number of appendices, giving the analysis and commercial treatment of complex ores of vanadium and uranium, tungsten and molybdenum, and tests for some of the more common metals.

The work contains much information, such as could be obtained only by a diligent search through large works on chemistry, and in addition many items of recent appearance, and many which are here printed for the first time. The commercial information given is reliable and much more practical than is usually found in chemical works. One feature, from the scientific point of view, is the entire absence of references to other works, or to the literature of the subject, and therefore, as a necessary consequence, the inclusion of all absolutely necessary details. This characteristic of the work makes it the more valuable to persons who do not read French and German, or who do not have access to a scientific reference library, and of less value to those who *can* get at the original sources of information. The book is therefore to be particularly recommended to the commercial and practical man, and to the scientist out of touch with a large scientific library.

Introduction to the Rarer Elements. By Philip E. Browning, Ph. D. New York: John Wiley & Sons, 1903. 157 pages. Price $2.50.

This work is prepared from material used by the author in giving a short lecture course at Yale University, and is intended as an introduction to the study of those elements not always taken up in a general course in chemistry. The elements treated of are (with the exception of five pages given to the newly discovered gases of the atmosphere) identical with those catalogued by Dr. Ohly (see previous review), and the order of treatment is to give for each element its discovery, occurrence in nature, methods of extraction of its salts in the laboratory, preparation of the element, properties, characteristics of its compounds, quantitative estimation and separation from other elements. Under each of these headings the information given is comparatively brief and lacks detail to such an extent, particularly in the analytical portions, as to be comparatively useless as a practical guide to work by. The lack of detail alluded to is partly compensated for by numerous references to the original articles, to which the student or investigator may refer for actual details of manipulation, but this reduces the practical value of the information actually given from the rank of a hand-book to that of an index.

The book is, therefore, in one way, a valuable introduction to the further and more complete study of these elements. The lack of detail is a sharp limitation on the value of the work, which would not be felt so much by the reader who had at his elbow a good chemical reference library, but which would render the book practically valueless to the isolated chemist or metallurgist not so provided. To the student in the laboratory, or the investigator well equipped with works of reference and having access to files of the chemical journals, the book is full of valuable information and rich in suggestions of further study.

ELECTROPLATING DYNAMOS.

In our February issue, 1903, page 230, we gave an illustrated description of electroplating dynamos built by the Holtzer-Cabot Electric Co., of Boston, Mass. From an interesting and neatly illustrated bulletin (No. 146), issued recently by this company, we gather the following additional information.

The table given below gives particulars as to the standard sizes of plating dynamos built by the Holtzer-Cabot Co. All machines are provided with a combined oil pan and sub-base with belt-tightening device. A suitable pulley and field regulator is also furnished with all machines. The E 1-6 and No. 1 and 2 platers generally supply single tanks, so the shunt winding is used to secure simplicity; on the larger units, however, compound winding is used. These machines are wound for 6 volts at the speeds given, although in any case a range of from 4 to 8 volts may be obtained by field and speed manipulation. Voltages outside of the limits named are to be obtained by special windings. Separate excitation is earnestly recommended on all of these large machines, even if it involves the use of a separate exciter, since in this way the simplicity of a shunt machine is secured with the voltage stability of a compound machine. The machines are usually belted and run at a speed which is purposely made low to do away with as much of the friction loss as possible, and also to prevent the brushes from cutting the commutator, a difficulty often encountered in high-speed machines of this type. The two halves of the armature deliver their outputs in parallel to the terminal blocks at the full voltage of the machine.

Size No.	H. P. Required to Drive.	Approx. Speed.	Number of Poles.	Output in Amperes at 6 Volts.	Sq. Ft. per Hour.			No. Gals.			Pulley	
					Nickel.	Brass or Copper.	Silver.	Nickel.	Brass or Copper.	Approx. Shipping Weights.	Diameter.	Face.
E 1-6	¼	1800	2	20	6	3	10	80	40	100	2	1¼
1	½	1300	2	35	12	5	17	140	70	200	2	2
2	⅞	1200	4	65	24	9	37	260	125	250	3	2
3	1½	1000	4	125	41	18	62	500	500	400	4	2½
4	2¾	900	4	250	83	35	125	1000	400	700	5	3
5	4¼	800	4	400	133	57	200	1600	750	1000	6	3
6	7	700	6	700	233	100	350	2800	1200	1400	7	4
7	9¾	650	6	1000	333	143	500	4000	1800	1700	8	5
8	12½	600	8	1400	466	200	700	5600	2700	2000	10	6

It is, of course, impossible to give more than a general idea of the size required for certain purposes. The figures given here relate to a salt solution in the case of the nickel, and acid solution in the case of the copper, both of rather a low density. The distance between electrodes was about 4 inches, and the work was a plain surface of brass, one square foot in area. The plate was .0004 of an inch in the case of the nickel and .001 of an inch in the case of the copper, the time being one hour in each case. The temperature was 70° F. and the deposit was purposely made of a finely grained nature, such as is used in buffed work. A modification of any of the conditions named would cause some variation in the quantity of current required, so that the data here given will serve as a guide only in a very general way.

The dynamo should, if possible, be placed in a clean, cool and dry place. It is, of course, advisable to place the machine as near the tanks as possible, but never in an elevated position where it will be subjected to the fumes from the tanks. It is well to have a good tight partition between the plater and the plating room. The machine should be set on a substantial foundation, and all vibration eliminated, if possible. Care in this respect will add to the life of the machine.

GRINDING ORES.

Electrometallurgy is the most recent branch of metallurgy and may justly be considered to be still in its infancy. But the rapidly increasing use of the electric current for power purposes in a metallurgical plant will surely lead to an increasing use of electrochemical methods in metallurgy; the distinct and undeniable advantages which electrochemical methods possess for certain work in metallurgy, are quite evident, and it is certain they will more and more be taken advantage of when electric current is already available in a plant for other purposes, such as power and lighting. It is generally at a rather late stage that electrochemical methods enter into a metallurgical process; what Nature gives us, are ores, and they must

first undergo a mechanical and chemical treatment before they are ready to be dealt with by an electrochemical method. The success of an electrochemical method often depends upon a judicious and suitable preliminary treatment by mechanical and purely chemical means.

The simple process of grinding ores is one of the first and most important in any metallurgical process, and for this reason our readers will be interested in the following description of the Kent Mill, made by the Kent Mill Co., of New York, which, while in extended use in metallurgical plants in general, has also already found successful application in connection with electrometallurgical works.

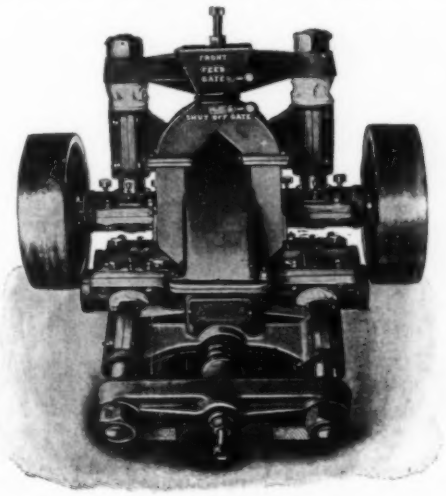


FIG. 1.—KENT PULVERIZER.

The Arlington Copper Co., of Arlington, N. J., have installed two Kent mills for grinding the ore to 20 mesh through these mills; the ore is then roasted and undergoes a chemical treatment, and is then passed to the electrolytic vats for producing a high-grade electrolytic copper.

In cyaniding processes—whether in the final step the gold is precipitated by zinc shavings or by electrolysis—the pulverizing of the ores so as to give a uniform powder suitable for subsequent treatment is of the greatest importance. The Helena Gold Mining Co. uses the Kent mill in connection with a cyaniding plant, and have found its adaptability for this class of work thoroughly satisfactory.

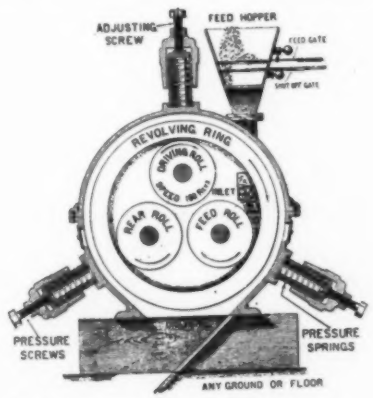


FIG. 2.—INTERIOR OF KENT MILL.

Figure 1 shows a Kent quartz pulverizer for grinding any quartz, ores, cement, phosphate rock, etc. The interior of the Kent mill, as shown in Fig. 2, consists essentially of a revolving ring and three rolls pressing against its inner face; these are the only four wearing parts; the rolls are convex, and the ring is concave and tracks on the rolls. The rolls are supported yieldingly by means of springs and the rolls again support the ring. In this way the four crushing parts are free to move to pass iron or uncrushable objects, and are cushioned to take up shock and vibration and prevent crystallization or breakage.

The rock falls from the inlets onto the inner face of the ring. Centrifugal force holds it there in a layer an *inch deep*. It revolves with the ring, and passes under the rolls. The rolls are pressed by the springs outwardly against the rock on the ring with a pressure adjustable to 20,000 pounds by the screws against the springs. The rolls roll over the rock, crushing it against the ring. The crushed rock flows off each side of the ring into the casing and falls to the discharge.

The body of rock between the rolls and the ring makes 90 per cent of the rock abrade on itself in crushing, thus reducing the wear on the wearing parts enormously.

REAGENT BOTTLES WITH INDELIBLE LETTERS.

Messrs. EIMER AND AMEND, of New York City, have been appointed sole agents for *Stender Reagent Bottles*, the only make in the world whose black letters are guaranteed to be absolutely indelible against any reagent.

PERSONAL.

Prof. WILHELM OSTWALD, of Leipzig, the famous German chemist whose biographical sketch and portrait were published in the February number of ELECTROCHEMICAL INDUSTRY, delivered an address in German at the recent opening of Prof. Jacques Loeb's newly built biographical research laboratory at Berkeley, Cal. Prof. Ostwald is now touring this country, and intends to sail again for Europe in the middle of September.

Dr. W. H. WALKER, of Boston, Mass., has now returned from Europe, where he attended the Fifth International Congress of Applied Chemistry, of which he was elected a vice-president. Dr. Walker also visited various electrochemical plants to study recent electrochemical developments abroad.

Mr. WILLIAM J. HAMMER, whose very elaborate lecture on radio-active, phosphorescent and fluorescent substances, on the properties of selenium and on the treatment of disease by ultra violet light, was received with such profound interest at the joint meeting in April of the American Institute of Electrical Engineers and the American Electrochemical Society, has received a cordial invitation from the *Faraday Society* to deliver a similar lecture before this society in London.

INDUSTRIAL NOTES

The firm of J. BISHOP & Co., refiners of platinum, whose plant at Sugartown, Pa., was destroyed by fire on January 30 last, have erected a new plant at Malvern, Pa. The new building is a commodious two-story brick structure with increased facilities for supplying platinum sheet and wire in all forms for special purposes. The concern is one of the oldest in this line in this country, having been established in 1842.

We have received from the WESTINGHOUSE ELECTRIC AND MANUFACTURING Co. circulars No. 1067 on air blast transformers and 1037 on engine-type alternators.

The neat and profusely illustrated catalogue of Assayers' and Chemists' Supplies for 1903, issued by the DENVER FIRE CLAY Co., of Denver, Col., contains on the first 206 pages a very complete list of general chemists' and assayers' laboratory supplies; twenty-four more pages deal with special chemical apparatus for analytical work, and the balance of the catalogue (70 pages) with outfits for assayers and prospectors, school sets of chemical apparatus; collections of minerals; models and charts; scientific books; fire brick and fire clay material; and chemicals and pure reagents.

DIGEST OF U. S. PATENTS

PRIOR TO JULY, 1902.

Compiled by Byrnes & Townsend,
Patent Lawyers,
National Union Building, Washington, D. C.

WHITE LEAD BY ELECTROLYTIC METHODS.

292,119. January 15, 1884. Johann K. Kessler, Milwaukee, Wis.

The electrolytic tank is divided by an impervious partition extending from the bottom nearly to the top; electrolyte consists of a solution of sodium or potassium acetate filling both compartments. The anode, consisting of lumps of lead, is placed upon one side of the partition, a body of lead serving as the cathode being placed in the other compartment. Upon passing the current, lead acetate and the alkali hydroxide are formed in the respective compartments; these are mixed in a separate vessel, precipitating hydrated lead oxide. This is maintained in suspension by an agitator and carbon dioxide injected. The precipitate of white lead is filtered off, washed and dried and the regenerated solution returned to the electrolytic tank.

292,753. January 29, 1884. Johann K. Kessler, Milwaukee, Wis.

A square vat is filled with an alkali metal acetate solution and provided with a central carthode of sheet lead, around which are grouped the lead pigs constituting the anode. Spongy lead is electrodeposited on the cathode and from time to time removed, washed and pressed, and carbonated by a mixture of air, steam and carbon dioxide. The white lead so produced may be converted into red lead by the action of air at red heat.

359,352. March 15, 1887. Edward V. Gardner, London, Eng.

To convert blue lead into white lead exposes it to commingled vapors of acetic water and air. The basic acetate and hydrate formed are subsequently carbonated by carbon dioxide. The action is accelerated either (1) by placing electro-negative substances in contact with the lead; for instance, the lead may be supported on carbon grids; the electro-negative material may be in the form of carbon or may be platinized; (2) by passing electric discharges through vapors either in chamber or before entry; (3) by using ozonized air.

414,935. November 12, 1889. Turner D. Bottome, Hoosick, N. Y.

Electrodes of lead in solution containing 6 per cent each of sodium and ammonium nitrates and maintained saturated with carbon dioxide. C. D. 15 amperes per square foot anode surface; temperature 16° G. Carbon dioxide continuously injected and water added as required.

442,661. December 16, 1890. Turner D. Bottome, Hoosick, N. Y.

Desilverizes lead with production of white lead. The argentiferous lead anodes are immersed in solution composed of 3 per cent each ammonium nitrate and carbonate, carbon dioxide being continuously injected. The lead is said to be precipitated as basic carbonate, while the silver is deposited in metallic state on the cathode.

459,946. September 22, 1891. David V. Kyte, Indianapolis, Ind.

Argentiferous lead anodes are immersed in a solution of an acid capable of forming a soluble salt, preferably 300 cc of pure nitric acid to two liters water, but mentions also as suitable acetic, hydrochloric, sulphuric, carbonic, oxalic, tartaric and citric acids. Passes current (10 amperes per square foot anode surface) until solution is saturated with lead, then substitutes carbon anode and silver cathode and precipitates silver as metal. Removes electrodes, carefully neutralizes solution by sodium or potassium hydrate and injects carbon dioxide to precipitate white lead; or may neutralize solution by alkali metal carbonates. Claims larger yield by reason of the slight solubility of the basic salt in the neutral electrolyte.

496,109. April 25, 1893. Arthur B. Browne, Cambridge, Mass.

Pig lead anodes supported on a grid, electrical contact being made through a skeleton frame of aluminium. Cathode is lead-faced wooden block supported above anodes. Sodium nitrate or acetate is introduced below anodes. Anode and cathode products react to form hydrated oxide of lead, which is transformed into carbonate by being permitted to dry in air or in atmosphere of carbon dioxide.

527,830. October 23, 1894. Arthur B. Browne, Cambridge, Mass.

White lead produced by process of United States patent 496,109, has a yellow tinge, which is attributed to organic matter aided by mordanting action of aluminates formed at cathode. To obviate color subjects the lead hydrate to the action of an alkali carbonate solution while the former is still moist, thereby dissolving out coloring matter and partially carbonating. The hydrate thus purified is washed and carbonated as in 496,109.

551,361. December 17, 1895, and 555,232, February 25, 1896. Arthur B. Browne, Cambridge, and Edwin D. Chaplin, Natick, Mass.

Apparatus and process respectively for continuous production of white lead. A series of electrolytic cells, each provided with lead anodes and any insoluble conductors as cathodes is employed. A solution of sodium nitrate as electrolyte flows through like compartments of all cells in succession. Anode and cathode solutions are mixed in separate vessels, the precipitated lead hydroxide filtered off and converted into carbonate by sodium carbonate. Resulting white lead separated by filtration and dried.

560,518. May 19, 1896 Jules Meyrueis, Paris, France.

Caustic soda from electrolytic cell is admitted to boiler containing litharge; the hot solution is drawn off and carbonated to precipitate white lead. Resultant alkaline solution withdrawn and further carbonated to form sodium bicarbonate, the mother liquor being returned to the electrolytic cell.

563,553. July 7, 1896. Arthur B. Browne, Cambridge, and Edwin D. Chaplin, Natick, Mass.

Substantially the same process as United States patent 555,232, excepting that two pervious diaphragms are employed and the electrolyte is introduced between them; a somewhat higher solution level is maintained between the diaphragm to prevent diffusion. Instead of a lead anode a carbon anode may be used, the lead to be dissolved being placed adjacent thereto. Nitric acid is added either continuously or at intervals to dissolve crystals of basic lead nitrite, which tend to form in anode compartment.

563,554. July 7, 1896. Arthur B. Brown, Cambridge, and Edwin D. Chaplin, Natick, Mass.

Caustic soda solution electrolyzed with lead anode in positive compartment of a cell provided with a diaphragm, thereby forming brown oxide of lead, which is dissolved in caustic soda. The resulting plumbate is neutralized by carbon dioxide precipitating white lead. The caustic soda and carbon dioxide are derived from the cathode and anode compartments, respectively, of an electrolytic cell supplied with a solution of sodium carbonate.

563,555. July 7, 1896. Arthur B. Browne, Boston, Mass.

Improvement on 563,553. Finds that if electrolyte between diaphragms be maintained by circulation below a certain degree of alkalinity diffusion of hydrate into positive compartment is prevented and no necessity arises for adding an oxidizing agent. This specification states the equations in accordance with which the production of white lead is presumed to take place.

The balance of this class of patents will be dealt with in our next issue.